# Study on Hydrogen Absorption Properties of U-55ZR Alloy

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The development of materials with high hydrogen storage capacity is one of the key issues for practical applications in hydrogen energy systems. The uranium-zirconium alloy is a promising material for hydrogen storage. In order to develop new hydrogen storage materials, hydrogen absorption properties of zirconium-rich alloy of 55 wt.%Zr (U-55Zr) were examined at temperatures from 350 to 600°C and at a hydrogen pressure slightly lower than one atmosphere. Hydrogen-absorption isotherms were measured at 350, 400, 500 and 600°C. The hydrogen absorption measurements have been made on four alloy specimens in a SETARAM SETSYS EVOLUTION 24 thermo balances by thermo-gravimetric (TG) analysis. The U-55Zr alloy was prepared from the constituent elements by powder metallurgy using depleted uranium and sponge zirconium and studied in as cast condition as hydrogen storage material. Microstructure investigations were conducted for the starting alloy specimens and hydrogenated specimens using a scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS). Crystal structures of the specimens were also analyzed with X-ray diffraction technique. The hydrogen capacity of U-55Zr alloy was determined by weighing the samples prior to and after the hydrogenation process. The kinetic of hydrogen absorption related to the hydride composition was analysed and discussed.

Keywords: hydrides, hydrogen storage, U- alloys, kinetics

During the last decades hydrogen has attracted a worldwide attention as a powerful energy carrier. The fusion reactor engineering demands the safe handling of hydrogen isotopes. In this context, the solid state storage of hydrogen isotopes in the form of metal hydrides is considered the safest and the most advantageous method [1]. Depleted uranium is one of materials highest hydrogen storage capacity. Hydrogen absorption properties of depleted uranium are suitable for tritium storage [2-4]. It easily absorbs hydrogen below 300°C to form UH<sub>a</sub>, but it disintegrates into powder because of the enormous volume expansion on hydrogenation [5] which is high pyrophoric [6] and has a high possibility of contamination. In the field of alternate materials development, substantial progress has been made during a few decades such as development of uranium based alloys, which shows improved properties over uranium. Hydrogen absorptiondesorption properties of various uranium alloys (U-Ti, U-Zr, U-Mo, U-Ni) have been studied [7-21] in order to find alloys with improve powdering capacity or low-powdering. Among these alloys, U<sub>2</sub>Zr, UZr<sub>2</sub> [12-14] and U<sub>2</sub>Ti [8, 14, 19, 21] were reported to show an excellent durability to powdering. Such alloys should have superior hydrogen absorption-desorption properties as uranium, such as high hydrogen absorption capacity, low dissociation pressure at 25°C, and have low powdering tendency as well as low pyrophoricity.

The study reported by Asada *et. all.* [17] reveal that the pyrophforicity of Zr or Ti rich uranium alloys is moderate than of U-rich alloy. Yamamoto *et. all.* [19] reveal that the maxim hydrogen absorption capacity for  $U_2$ Ti and UZr<sub>2.3</sub> alloys are found to be x=7.6 and x=7, respectively. Alloying U whit Zr or Ti keeps the equilibrium pressure of UH<sub>3</sub>, while powdering is greatly reduced, in the case of high content of Zr or Ti [20].

For hydrogen storage applications, is essential to generate data on the measurement of the maximum

hydrogen capacity and absorption and desorption conditions, necessary for comparison to other metal hydride systems. In this study the hydrogen absorption properties of a zirconium-reach of 55 wt.%Zr (U-55Zr) were examined in order to develop a new material for hydrogen storage.

# **Experimental part**

# Alloy preparation

The U-55Zr alloy (fig. 1) was prepared from the constituent elements by powder metallurgy using depleted uranium U<sup>238</sup> (<0.72%U<sup>235</sup>) of 99.0% purity and zirconium sponge of 99.8% purity, both of nuclear grades. Powder metallurgy involves the conversion of base metals in powder hydrides form, their mixing up and sintered at 1300°C, for 3 h. For alloy preparation amount of zirconium was adjusted against the weight of the uranium. The raw materials dosage (uranium, zirconium), loading/downloading of the hydrogenation furnace with the raw materials, grinding of zirconium hydrides, weighing of the powdery hydrides, dosage and mixing of the powdery hydrides, the isostatic pressing, the sintering of the loading from furnace, was carried in the chain of boxes with argon circulation [22]. Four samples from ~1.2 cm in diameter and ~2 mm in thickness were cut from the as-cast alloy. Each sample was used for hydrogen absorption



Fig.1. U-55Zr alloy (sintered rod) prepared by powder metallurgy route

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measurements in order to perform the hydrogen experiments, carried out in a thermal-gravimeter (TG) analyzer. No special treatment (annealing, quenching, etc) was conducted to the specimens before hydrogenation.

### Alloy characterization

Microstructure observation was conducted for the starting alloy specimens and hydrogenated specimens using a scanning electron microscopy (SEM), TESCAN VEGA II LMU equipment, equipped with secondary (SE), backscatter electron detectors (BSE) and energy dispersive X-ray spectroscopy (EDS) system. SEM specimens were prepared by embedding samples in epoxy and polishing to achieve flat and smooth surfaces for examination. No etching was done on the samples. The homogeneity of the alloy was investigated at different morphological positions by EDX and elemental mapping. The phase composition of the alloy was assessed using X-ray diffraction technique (XRD) on a X Pert Pro MPD diffractometer, prior to and after hydrogenation. It was possible a qualitative and semi quantitative analyze of the samples. The XRD pattern was recorded with 2q range of 20°÷100° using CuK,  $(\lambda = 1.5406A)$  radiation, then the XRD patterns were evaluated and compared to JCPDS-Joint Committee on Powder Diffraction Standards, standard diffraction database[23].

# Measurements of transition temperature

The Differential Scanning Calorimetry (DSC) experiments have been carried out for pure uranium and U-55Zr alloy. The TGA-DSC 1600 rod supplied by SETARAM SETSYS EVOLUTION 24 thermo balance was used for phase transformation studies. To convert the heat flow signal from mV to W the DSC rod was prior calibrated using standards covering the temperature range  $(25 \div 1000^{\circ}C)$ . Temperature calibration of DSC rod was carried out by standard reference materials Sn, Zn, Al and Ag. All the experiments were carried out under purified argon atmosphere. DSC profile of samples was taken at 10 °C min<sup>-1</sup> both in the heating and cooling directions.

# Hydrogen absorption experiments

The hydrogen absorption properties of the prepared alloy were examined at various temperatures between 350 and



Fig.2. Apparatus used for hydrogen absorption experiments

600°C and a hydrogen pressure of one atmosphere. The hydrogen absorption measurements have been made on four alloy specimens in SETARAM SETSYS EVOLUTION 24 thermo balance (fig. 2). The temperature was measured by a Pt-PtRh10% thermocouple and the hydrogen absorption progress was constantly recorded.

The measurements of weight gains of the samples performed in situ. table 1 presents the parameters and results of hydrogenation process for four specimens.

# **Results and discussions**

Structural, micro structural characteristics

According to the Zr-rich part of U-Zr phase diagram [24], is easy to find that the choice of the present alloy compositions encompasses the eutectic line. From U-Zr phase diagram at 606°C, it is observed that  $\gamma(U, Zr)$  decomposes into  $\alpha$ -Zr and  $\delta$ -UZr, intermetallic phases.

The resulting diffraction pattern is shown in figure 3. Phase identification of alloy is confirmed by comparing their pattern with JCPDS files [23]. The XRD pattern for U-55Zr alloy clearly indicates that the major phase for this alloy composition was  $\delta$ -UZr<sub>2</sub> phase, an ordered compound of uranium and zirconium with a hexagonal lattice (file no. 01-073-2630) with some small amount of uranium and zirconium (file no.01-073-2630, 01-071-3958 respectively). No detectable quantity of oxygen pick up was observed in the sample. This was confirmed by absence of any oxide peak in the XRD pattern of the alloys. The SEM (BSE mode) images and EDX spectrum of U-

The SEM (BSE mode) images and EDX spectrum of U-55Zr alloy are shown in figure 4. The U-55Zr alloy was

Specimen.	Initial	Temperature	Reaction time	Heating rate	Weight
No.	weight	(°C)	(h)	(°C/min)	Difference
	(g)				(mg)
UZr-1	0.70960	350	21	20	24.20
UZr-2	1.69640	400	21	20	23.266
UZr-3	1.59177	500	21	20	20.082
UZr-4	2.09979	600	24	20	23.182



Table 1THE PARAMETERS AND RESULTS OFHYDRIDING PROCESS

Fig.3. X-ray diffraction pattern of U-55Zr alloy



Fig.4. Backscattered electron photomicrograph of as cast U-55Zr prior to hydrogenation (left); EDS spectrum (right)



examined under BSE mode in order to generate contrast based on the average atomic number in each phase. As can be seen in these pictures, the morphology of U-55Zr showed two distinct phases: the  $\alpha$ -Zr phase (in dark gray regions) and  $\delta$ -UZr<sub>2</sub> phase (in light gray regions) and a small amount of uranium. The  $\alpha$ -Zr phases are distributed in the d-UZr<sub>2</sub> phase. It is in accordance with the XRD results. Also, small amounts of pores are found throughout the sample. Pores are thought to originate, because hydrogen gas is embedded in the surface of zirconium powders and a little remaining hydrogen gas isn't emitted during sintering [25]. U-55Zr alloy composition prepared for the experiment found through EDS is reported in table 2.

Figure 5(a) shows a SEM image with two specified regions (fig.5(b), fig. 5(c), respectively) from which EDS spectra were acquired, labelled P1, P2, P3. The corresponding EDS spectra are displayed in figure 6a and figure 6b, respectively. Each region corresponds to one of the X-ray diffraction results presented in the previous section. Figure 5(d) shows an X-ray map. This X-ray map, created from the characteristic X-rays emitted from each

 Table 2

 DETAILS OF SAMPLE COMPOSITION FOUND

 THROUGH EDS

Element	[wt.%]	[at.%]	Erorr [%]
Zr	58.2	78.41	2.3
U	41.80	21.59	1.8
0	0	0	0
Total	100	100	4.1

element upon excitation from the electron beam, depicts zirconium in red and uranium in green.

This microstructure was examined by energy dispersive X-ray spectrometer (EDS); the fluorescence spectrum was processed in the points marked on the picture, in table 3 being presented the results of elemental composition in each point analyzed. The spectrum was processed by Quantax Esprit 400 software with an automatic standard less method (PB/ZAF standard less).

The measured composition of the sample was analyzed in three different locations to find out weight percentage of U and Zr present and then average was taken as reported in table 3. The contrast from the backscattered electron image correlates directly with EDXS spectra where the bright phases are highly concentrated in uranium and depleted in zirconium and vice-versa.

Measurements of transition temperature using scanning mode

The measured start temperatures for U and U-55Zr alloy transformation are listed in table 4. Figure 7 shows the phase transformation temperatures. Very sharp transformation peaks associated with the heat effects of  $\alpha \rightarrow \beta$  and  $\beta \rightarrow \gamma$  transformation are clearly revealed for uranium. The U-55Zr alloy showed a heating transformation pertaining to  $\delta \rightarrow \gamma$  in DSC experiments.

#### Hydrogen absorption kinetics

Hydrogen absorption kinetics is an important parameter which is useful to the development of hydrogen storage materials for the practical applications. The hydrogen absorption kinetics of as-cast U-55Zr alloy has been investigated using thermo gravimetric technique, at constant pressure. The samples were heated to the test temperature and isothermal measurements were performed as a function of time. Four hydrogenation temperatures 350, 400, 500 and 600°C were used for investigation of the effect of hydrogenation temperatures.





Fig.6. EDS spectra from the identified regions in figure 5

	Fig. 5-c			Fig 5-b		
Element	P1, wt.%	P2, wt.%	P3, wt.%	P1, wt.%	P2, wt.%	<b>P</b> 3,
U	87.15	59.53	57.12	35.74	2.65	12.59
Zr	12.85	40.47	42.88	64.26	97.35	87.41
Total	100	100	100	100	100	100

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Table 3COMPOSITION DETAILS FOUNDTHROUGH EDS



The isothermal curves obtained at all the four temperatures, are shown in the figure 8. The mass of the sample increases linearly with time and gains mass stability at equilibrium. The mass gain at 350°C was recorded higher than that of other higher temperature that could not be attributed to the large sample mass.

Since the samples masses in each experiment were not identical, the results were normalized in terms of mass. The progress of the hydrogen alloy absorption was measured as a function of time, for the given temperatures. The data of weight changes vs. time, produced by the analyzer for the temperatures examined were used as the basis, for the calculation of the fraction reacted ( $\alpha$ ) in time t, according to eq. (1):

$$\alpha = \frac{m_t}{m_o} \tag{1}$$

where  $m_i$  is the weight changes after time *t*, seconds, and  $m_0$  is total weight change quantity after complete hydrogenation. The reacted fractions  $\alpha$ -t kinetic curve derived from the mass gain data and plotted figure 9.

The experimental a vs. t data were linearly fitted. The fitting equation is considered as the indicative of actual reaction mechanism to describe the hydrogen absorption process. The slopes of the linearity fitted curves gave the kinetic coefficient k (gave the rate constants) at these four temperatures. The kinetic parameters of isothermal experiments are given in table 5.

The hydrogen capacity (H/U+Zr) were determined by weighing the samples prior to and after the hydriding process and are listed in table 6. There are slight difference



Table 4

MEASURED TRANSFORMATION START TEMPERATURES OF U AND

**U-55Zr ALLOY IN HEATING** 

 $T_{f}$ 

(°C)

684

Peak

area, A

(µVs/mg

0.5894

Fig.8.The absorption curves for uranium alloy samples under isothermal conditions





in the H/(U+Zr) ratio among the specimens. The literature data [20] shows that on hydrogenation, U-Zr alloys decompose into UH<sub>3</sub> and ZrH<sub>x</sub> (x<2) phases ad the hydrogen capacity for UZr, is 6.5.

Initially, at a hydrogen pressure of one atmosphere at 600°C, U-55Zr absorbed an amount of hydrogen. Then by decreasing the temperature stepwise by 100°C steps, the hydrogen concentrate increased and the specimen not disintegrated into fine powder.

Samples	Temperature	Kinetic	Weight Difference	Fitting
	(C°)	coefficient	(mg)	correlation
		Kx10 <sup>-4</sup>		coefficient
				$\mathbb{R}^2$
UZr-1	350	5.9856	13.732	0.994
		1.7193	24.546	0.990
UZr-2	400	3.5821	21.397	0.999
		1.3795	23.150	0.998
UZr-3	500	5.4629	18.206	0.998
		0.3570	20.233	0.996
U-Zr-4	600	5.1332	20.315	0.999
		0.6057	23.158	0.994

 Table 5

 THE RESULTS OF ISOTHERMAL ANALYSIS





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# Structural, micro structural characteristics after hydrogenation

In order to unravel the hydriding behavior of U-55Zr, structural (x-ray diffraction, XRD) and microstructural (scanning electron microscopy, SEM) characteristics were caried out.

Figure 10 shows the SEM images of U-55Zr alloy after hydrogenation. After hydrogenation, no specimens disintegrated on hydrogenation. Secondary cracks can be observed in all directions, indicating the presence of very high internal stress in the crystalline network. The cracks are larger inside dark regions which represent a compound of uranium with zirconium with an atomic number lower than the rest of the matrix. The hydrogen is absorbed in greater amount in this compound, making thus possible a changing in the crystalline network. As the temperature is not appropriate for the formation of uranium hydride, we suppose the compound is zirconium hydride or the hydride of zirconium alloy.

Figure 11 shows observed phases in the X-ray diffraction patterns of hydrogenated specimens. After hydrogen absorption, X-ray diffraction proved that samples have a heterogeneous composition. A clear ternary hydride was not identified.

From X-ray diffraction patterns of the specimens hydrogenation between  $400 \div 600^{\circ}$ C, the ZrH<sub>v</sub> (x=1.5÷2) phase was identified as main phase. No peaks from uranium hydride were observed. Here Zr was expected to be hydrogenation to ZrH, by a rapid reaction. However, in the X-ray pattern of the specimen hydrogenation at 350°C, the peaks of UH, and ZrH, were identified in addition to several unknown peaks most probably attributable to the ternary hydride. All the peaks were broad. It probably shows a significant deviation in the lattice constants due to the difference in the hydrogen concentration.

Hydrogen concentration of U-55Zr alloy is larger than that of Zr in the temperature range 350-600°C. Consequently, U-55Zr alloy can hold more hydrogen that U or Zr at the same temperature. This fact gives an attractive advantage if it is used as a material storage.

#### **Conclusions**

Hydrogen absorption properties of U-55Zr alloy of four different samples were examined to search a possibility for this material to be used as a new hydrogen storage material. For all the specimens, hydrogen capacities were similar to or higher than that of UH, or ZrH, hydrides. The samples consisted of two main phases before

Table 6 THE HYDROGEN CAPACITY OF U-55Zr

Fig .10.SEM images of the U-55Zr alloy after hydriding

Fig.11. Combined diffraction patterns of U-55Zr after hydrogenation

hydrogenation and a few hydride phases after hydrogenation. A clear ternary hydride was not identified. It is possible that the ternary hydride to be a mixture of UHx and ZrHx [14].

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