EVALUATION OF PHYSICAL STABILITY OF THE U-ZrH SYSTEM

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Stabilitatea fizică a combustibilului alcătuit din aliajul uraniu-hidrură de zirconiu a fost studiată prin intermediul unor măsurători simultane de termogravimetrie şi analiză termică diferenţială (TGA-DTA). Combustibilul alcătuit din aliajul uranium-hidrură de zirconium este un sistem complet având şi rol de moderator, iar tehnologiile de fabricare s-au bazat pe metalurgia pulberilor. Studiile experimentale au constat în teste de ciclaj termic asupra sistemului uranium-hidrură de zirconiu (45% uraniu) în intervalul de temperatură 500-750°C. În timpul investigării termogravimetrice am observat pierderile de masă, iar eventuale efecte termice (transformari de fază) au fost înregistrate prin DTA. Transformările structurale şi morfologice au fost examinate prin difracţie de raze X şi microscopie electronică cu baleiaj (SEM), după 100 ciclii de încălzire-răcire. Scopul acestei lucrări este de a oferi date experimentale care furnizează informaţii necesare exploatării elementelor combustibile TRIGA, fabricate la INR.

The physical stability of uranium zirconium-hydride fuel has been studied by means of simultaneous measurements of thermo-gravimetric and differential thermal analyses (TGA-DTA). The uranium-zirconium fuel is an integral fuel-moderator system and the fuel manufactory technologies are based on powder metallurgy. The experimental studies consisted in thermal cycling tests on uranium-zirconium hydride (45 wt% uranium) fuel over the temperature range 500°C to 750°C. During thermo-gravimetric research, we noticed mass los and the thermal events occurring (the phase transformation) to the sample are recorded by DTA. Morphological and structural changes were examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM) after 100 heating-cooling cycles. The purpose of this paper is to describe the experimental data which supplies the information regarding the practical use of TRIGA fuel elements, fabricated at INR.

Keywords: Thermal cycling, uranium zirconium hydride, thermo-gravimetriy

1. Introduction

Hydride nuclear fuel (uranium zirconium-hydride) have been successfully in research reactors for many years [1,2]. TRIGA (Training Research Isotope

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production General Atomics) reactor is a Light Water Reactor, a well-known pool type reactor using uranium zirconium-hydride (U-ZrH). The development and use of U-ZrH fuel for the TRIGA reactor have been underway at General Atomic since 1957 [3], permitting them to successfully perform the unique transient power pulsing and allowing the reactors to operate worldwide for more than 45 years without any accident related to fuel over-heating [4].

The structure of uranium-zirconium hydride fuel consists of a separate metallic α-U phase dispersed into a solid zirconium hydride matrix (δ-$ZrH_{1.6}$). The H/Zr ratio is nominally 1.6 (in the face-centered cubic delta phase). Fig. 1 shows a photomicrograph of the fuel. The dark and light regions represent uranium and zirconium hydride phases, respectively.

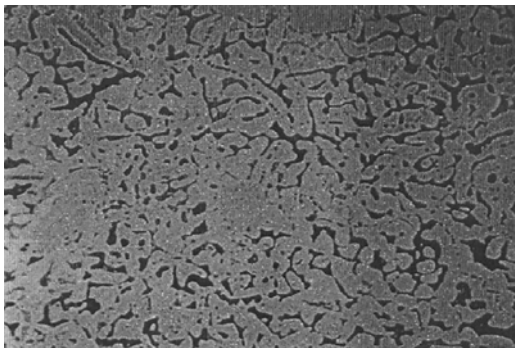


Fig. 1. Typical microstructure of the hydride fuel [4]

Institute for Nuclear Research (INR) Pitesti, Romania, operates a TRIGA dual–core research reactor. The dual-core concept involves operation of a 14 MW TRIGA Steady State research and materials testing reactor at one end of a large pool (300 cubic meters of water), and the independent operation of an annular core pulsing reactor (TRIGA-ACPR) at the other end of the pool (see Fig. 2) [5]. The design limits set for the high power TRIGA core [5] are fuel temperatures of 750°C at steady state and 1050°C under transients.

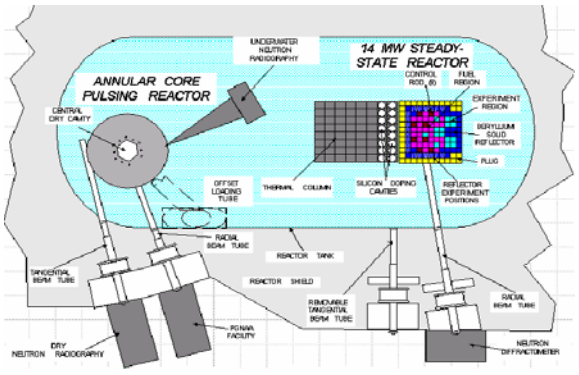


Fig. 2. INR Pitesti TRIGA dual–core Research Reactor, [5]

INR TRIGA reactor uses a fuel consisting in zirconium hydride ($ZrH_{1.6}$) rods in which uranium is distributed in the form of a dispersion of metallic particles having a size of about 5μm. The size of the uranium particles increases from 1 to 5 μm with uranium content enhance from 8.5 to 45 %wt. The fuel rods manufactory technologies are based on powder metallurgy. Powder metallurgy involves the conversion of base metals in powdery hydrides form, their mixing up and the sintering. The obtaining process of U-($ZrH_{1.6}$) fuel involved the manufacture of U-Zr alloy as intermediary product, which will be then subjected to a hydriding controlled process. The raw materials dosage (uranium, zirconium), loading/ downloading of the hydriding furnace with the raw materials, grinding of zirconium hydrides, weighing of the powdery hydrides, dosage hydrides powdery, dosage and mixing of the powdery hydrides, the isostatic pressing, the sintering of the loading from furnace, sensitive to oxygen, was carried in the chain of boxes with argon circulation.

The knowledge of thermo-physical properties of the nuclear fuel, have a great importance in the characterization of his behaviour in reactor. Changes under normal operating conditions can affect the geometry of the fuel and thermo-physical properties.

Data related to zirconium hydrides but also to TRIGA fuel thermo-physical properties are presented in Mueller [6] and Simnad [1] works.

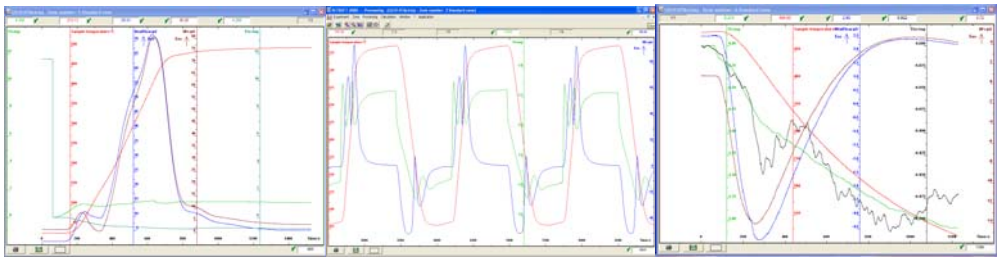
The main purpose of our work is to demonstrate the fuel stability for thermal cycling from ambient to operating temperatures.

2. Experimental set-up

The experimental studies consisted in thermal cycling testes from ambient conditions to operating conditions on U-$ZrH_{1.6}$ alloy by means of a simultaneous thermal analyser (SETSYS EVOLUTION 24) which allowed simultaneous differential thermal analysis (DTA) and thermo-gravimetric (TGA). The TGA-DTA 1500 rod was used. The samples used in the present investigation had the following elemental analysis: the uranium content was 45 %wt, the H/Zr ratio1.6 and the level of the oxygen content 3140 ppm. The content of 3600 ppm oxygen reported to zirconium is the upper limit that can be accepted for uranium-zirconium alloy rods [7]. The specimen of U-($ZrH_{1.6}$) was thermally cycled over

100 times in temperature range from 500 to 750°C and 1100 mbar. The heating rate for TGA-DTA analysis was 90 deg/min, under argon static atmosphere (see Fig. 3b).

Before thermal cycling, the sample was heated in an argon dynamic atmosphere with a flow rate of 20 ml/min in the temperature range from room temperature (RT) till 500°C, with heating rate 50 deg/min (see Fig. 3a). After the thermal cycling, the sample was cooled into argon dynamic atmosphere, with cooling rate 50 deg/min (see Fig. 3c). DTA-rod was prior calibrated using standards covering the temperature range (500÷750°C). For calibrating the DTA rod there is a facility using the standards so as to transform the electric signal S (in μV) into thermal power P (in mW). The blank of the heat flow signal was carried out under the same experimental conditions.



a) b) c)

Fig. 3. Experimental results at a constant heating and cooling rate

After TG-DTA measurements, the crystal structure and phase composition were investigated using a X Pert Pro MPD diffractometer, with CuKα radiation and λ=1.54178Å. The diffraction patterns (XRD) were measured for 2θ=20° to 80° then the XRD patterns were evaluated and compared to JCPC standard diffraction database. The sample was analysed before and after heating treatment. The morphology, the mean particle size and element distributions were observed by analysing a set images obtained in a Scanning Electron Microscope using TESCAN VEGA II LMU equipment. Visual inspection was done on Optical Microscope Karl Zeiss A Observer.

3. Results and discussion

Thermal cycling (see Fig. 4) tests were performed on 45 wt.% uranium fuel over the temperature range of 500-750°C, which includes the orthorhombic-to-tetragonal phase transformation at 652°C [8]. Simultaneous TGA and DTA analysis indicates the thermal behaviour of the product and mass loss during constant heating-cooling and measures both heat flow and weight changes as a function of temperature or time in a controlled atmosphere. While the physical

measurement of weight loss is obtained by TGA, the thermal events occurring (the phase transformation) to the sample are recorded by DTA. An upward peak represents for an exothermic event while a downward peak represent for an endothermic event on DTA curve. The results TGA-DTA analysis on U-$ZrH_{1.6}$ alloy are shown in Fig. 5. The temperature range from 500 to 750°C is associated with a loss of weight and strong evolution of hydrogen, after 25 cycles. Then, the release of hydrogen levels off quickly and tends to zero or a small increase. A weight loss of 6.07 %wt was observed under the endothermic process, thus indicated that sample released hydrogen gas. TG curves show that both endothermic peak have an associated mass loss and can only be related to hydrogen desorption processes. Differential thermal analysis showed that mass loss process is endothermic. During heating endothermic peaks of H_2 release accompanies desorption in the DTA curves. DTA curve show an endothermic peak at 592°C. The enthalpy value is 7.3505 J/g.

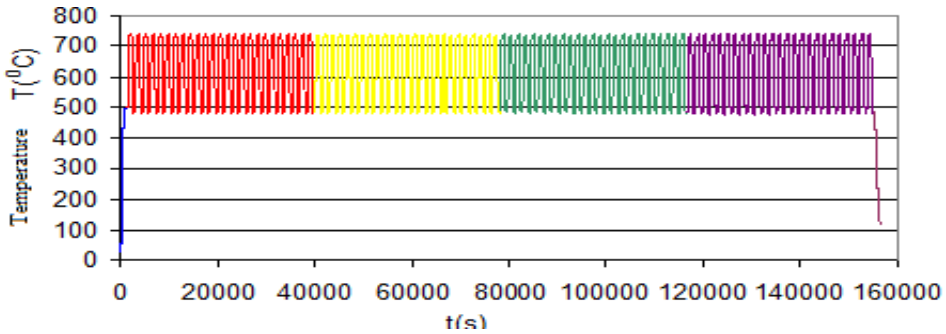
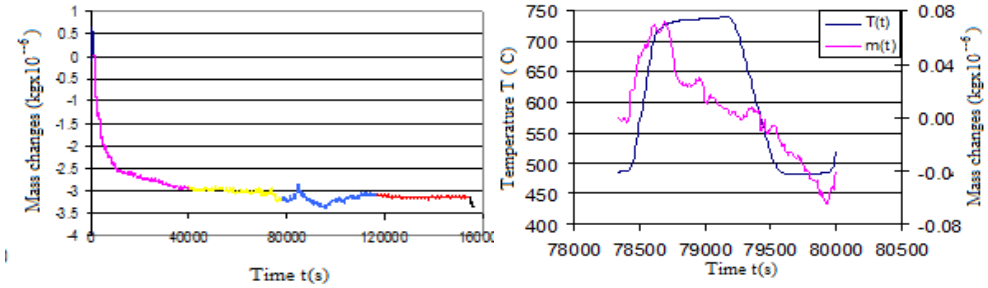


Fig. 4.Heating-cooling cycles



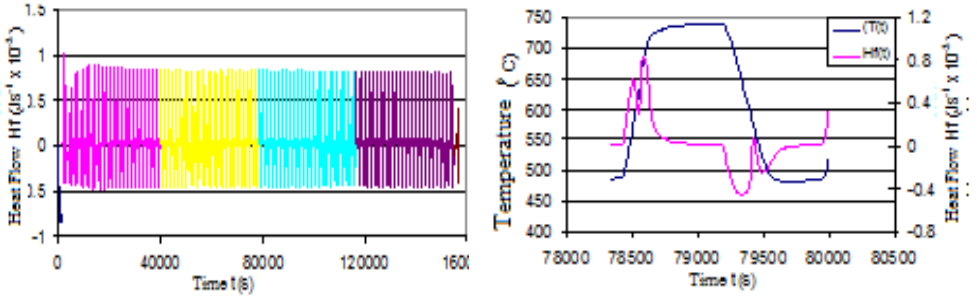
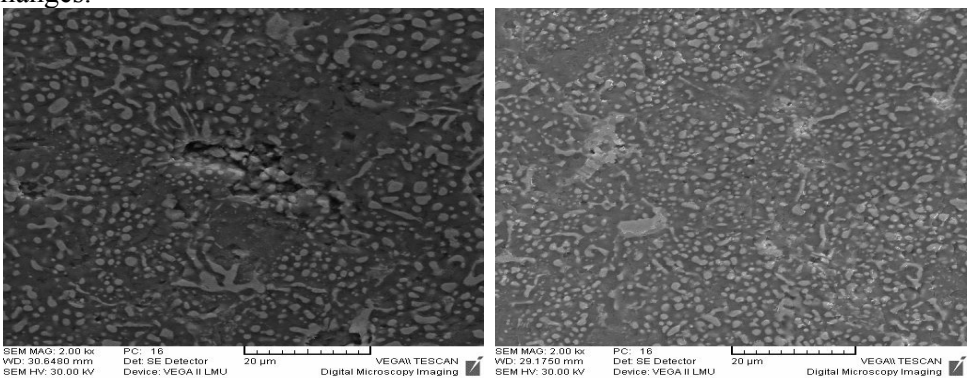


Fig. 5. TGA and DTA traces for U-$ZrH_{1.6}$

The morphology and microstructure were further investigated by scanning electron microscope (SEM) shown in Fig. 6. The average particle size of U is 1-5μm. The structure consisting of a fine dispersion of the uranium in a still largely zirconium hydride matrix precludes anisotropic growth from taking place as a result of cycling through the phase transformation temperature of the uranium It was observed from SEM analysis that the α-phase U (45%U, 20% enriched) of 1-5μm in grain size was uniformly dispersed in the bulk of δ- phase ZrH1.6, but it has segregated in the interdendritic regions of the cast structure. Some porosity and evidence of a second phase can be seen in these photomicrographs. Dark and light regions represent uranium and zirconium hydride phases, respectively. Structural and morphological analyses were made to determine the reason of mass changes.



a) *b)*

Fig. 6. Electron scanning microscope photos of U$ZrH_{1.6}$ system , before (left) and after (right) a number of cycles

The evolution of the X-ray diffraction patterns as a function of the thermal cycling for U-$ZrH_{1.6}$ is shown in Fig. 7. Fig. 7 shows X-ray diffraction patterns of U-$ZrH_{1.6}$, before and after thermal cycling. Following distinct phases were

identified: orthorhombic structure α-U [JCPDS 04-006-5474], tetragonal structure β-U [JCPDS 04-007-8575], but and $ZrH_{1.63}$ and $ZrH_{1.5}$ [JCPDS 04-004-8914, JCPDS- 04-008-1383]. The high-hydride composition eliminates the problems of density changes associated to the phase changes. The appearance of a small amount of monoclinic ZrO_2 [JCPDS 04-001-7279] and UO_2 [JCPDS 04-008-2456] around 2θ=28° is observed, probably due to the presence of oxygen. In various stages of this technology (powder metallurgy), oxygen contamination can occur influencing the quality of the final product. The presence of oxygen traces affects the rate of achieving the balance. Oxygen stabilizes alpha-phase hydride [7].

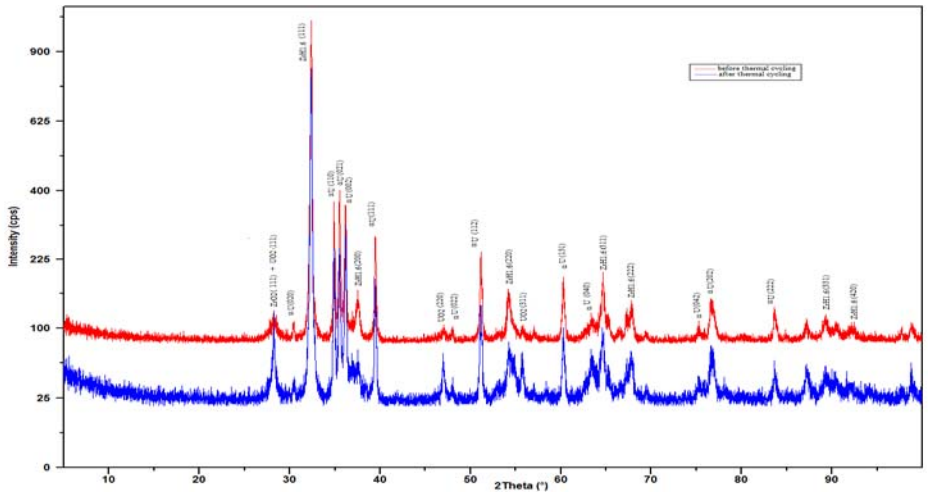


Fig. 7.X-ray diffraction of U-$ZrH_{1.6}$

4. Conclusions

The principal objective of paper is to demonstrate the fuel stability for thermal cycling from ambient to operating temperature.

Thermal cycling tests were performed on 45%wt uranium fuel over the temperature range of 500°C to 750°C, which includes the orthorhombic-to-tetragonal phase transformation at 653°C.

There were no significant changes and small decrease in weight was measured.

Thermal cycling tests show that the ZrH matrix stabilizes the fuel material such that it is dimensionally stable when repeatedly cycled through the uranium phase change temperature of about 680°C.

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