EXPERIMENTAL STUDY ON URANIUM ALLOYS FOR HYDROGEN STORAGE

M. DEACONU, T. MELEG, I. CIUCA, M. ABRUDEANU**, A. DINU, M. MIHALACHE*

Institute for Nuclear Research, Piteşti, Romania, mariea.deaconu@nuclear.ro
** University POLITEHNICA of Bucharest, Romania*
*** University of Pitesti, Romania*

ABSTRACT

The heaviest isotope of hydrogen is one of critically important elements in the field of fusion reactor technology. Conventionally, uranium metal is used for the storage of heavier isotopes of hydrogen (D and T). Under appropriate conditions, uranium absorbs hydrogen to form a stable UH_3 compound when exposed to molecular hydrogen at the temperature range of 300÷500°C at varied operating pressure below one atmosphere. However, hydriding-dehydriding on pure uranium disintegrates the specimen into fine powder. The powder is highly pyrophoric and has low heat conductivity, which makes it difficult to control the temperature, and has a high possibility of contamination Due to the powdering effect as hydrogen in uranium, alloying uranium with other metal looks promising for the use of hydrogen storage materials. This paper has the aim to study the hydriding properties of uranium alloys, including U-Ti U-Mo and U-Ni. The uranium alloys specimens were prepared by melting the constituent elements by means of simultaneous measurements of thermo-gravimetric and differential thermal analyses (TGA-DTA) and studied in as cast condition as hydrogen storage materials. Then samples were thermally treated under constant flow of hydrogen, at various temperatures between 573÷973K. The structural and absorption properties of the products obtained were examined by thermo-gravimetric analysis (TG), X-ray diffraction (XRD) and scanning electron microscopy (SEM). They slowly reacted with hydrogen to form the ternary hydride and the hydrogenated samples mainly consisted of the pursued ternary hydride bat contained also U or UO2 and some transient phase.

Key words: Hydriding, hydrogen storage, U alloys

Introduction

The development of hydrogen isotope storage materials with high capacity is one of the key issues for wide practical applications in hydrogen energy system [1]. Usually the most widely used and safest method of hydrogen isotope storage is solid state materials. The hydrogen storage behaviour of heavy metal uranium has been studied to some extent [1÷3]. Uranium easily absorbs hydrogen to form UH_3 compound at the temperature range 500÷700 K at varied operating pressure below one atmosphere and

the desorption pressure of UH_3 is adequately for holding hydrogen at room temperature and sufficiently high above 700K. In practical applications, however, it easily disintegrates into powder because of the enormous volume expansion on hydrogenation [4]. The powder is highly pyrophoric [5] and has a high possibility of contamination. Due to these disadvantages of using U, efforts have been made to improve hydrogen storage property by alloying [5÷9] with other metals. The uranium-titanium, uranium-molybdenum and uranium nickel alloys were selected in this research; its hydrogen absorption properties were investigated at hydrogen pressure as high as 1100 mbar and at temperatures between 573 and 973 K.

Experimental work

The UTi, UMo and UNi alloys specimens were obtained by melting the constituent elements by means of simultaneous measurements of thermo-gravimetric and differential thermal analyses (TGA-DTA) and studied in as cast condition as hydrogen storage materials. The elements used were depleted uranium pieces, surface cleaned before use and the alloying elements (Ti, Mo, Ni powder of 99.9% purity). The starting materials were mixed in required proportion and the melting was done at 1250°C, under argon atmosphere. In order to improve homogeneity, the initially prepared alloy was remelted several times.
After TG-DTA measurements, obtained alloys were characterized by X-ray diffraction for phase determination, where scan rate was kept at 1°/min. The theta standard XRD machine was used to generate XRD pattern. The source was CuKα and the tube voltage was 35.0 KV and tube current 30mA. The diffraction patterns (XRD) were measured for 2θ = 20° to 90° then the XRD patterns were evaluated and compared to JCPDS-International Center for Diffraction Data, standard diffraction database.
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.
The obtained alloys were then studied as hydrogen storage materials carried out in a thermal gravimeter (TG) analyzer. The samples were thermal treated under constant flow of hydrogen, for temperatures varying from 300°C up to 700°C and times of 1 to 70 hours, under the initial hydrogen pressure under one atmosphere. The progress of the hydrogen absorption was constantly measured as a function of time. No special treatment, such as annealing, was conducted to the specimen before hydriding.

Results and discussion

Simultaneous TGA and DTA analysis indicates the thermal behaviour of the product and measures both heat flow and weight changes as a function of temperature or time in a controlled atmosphere. Thermal cycles comprising heating and cooling ramps, were utilized to the observation of the melting and solidification point Temperatures and energies of reaction, showed as peaks in the heat flow curves were extracted directly from DTA curves. The results DTA analysis on uranium alloys are shown in **Figure 1**.

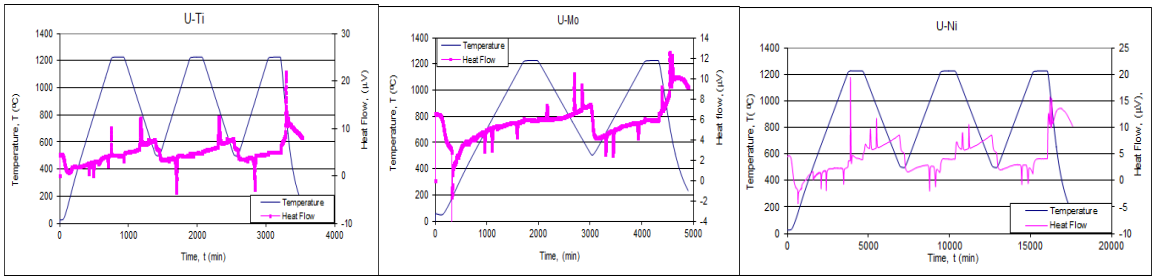

Figure 1 *DTA curves at different samples, 20 ℃/min heating rates*

The XRD pattern for uranium titanium alloy (U-Ti) prepared (as shown in **Figure 2**-left) clearly indicates that the major phase for this alloy composition was α-U with some small amount of UO_2, Ti and U_2Ti. The XRD pattern for uranium molybdenum (U-Mo) alloy shows the presence of major phase as α-U, Mo and U_2Mo (as shown in **Figure 2**, the centre). For uranium nickel alloy the major phases (as shown in **Figure 2**-right) are UNi_5 and Ni. The synthesis temperature during preparation of uranium alloys was kept well below the melting point of alloying elements and the expected metallurgical reaction is of solid state reaction type. Hence, the uranium alloys prepared by this method required to be remelted to get good homogeneous product. This was confirmed in the XRD patterns where oxide peaks were observed.

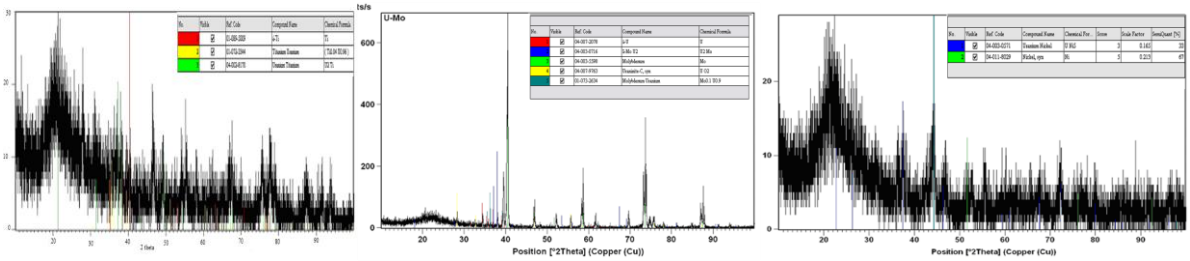

Figure 2.*XRD pattern of U-Ti (left), U-Mo (center), U-Ni (right) alloys*

The morphology of uranium-titanium alloy used in these investigations was characterised by Scanning Electron Microscopy (SEM) using a TESCAN VEGA II LMU operated at 10 to 20 kV.

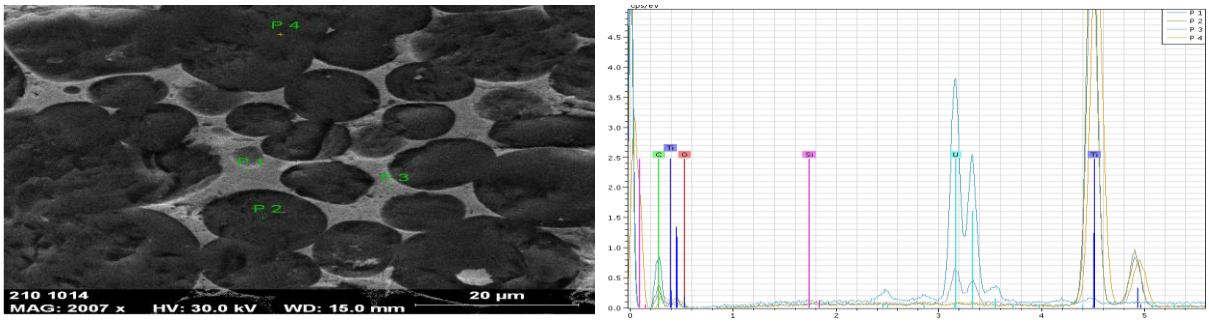

Figure 3 *SEM-EDX analysis of samples indicating the phase homogeneity and alloy composition*

The hydrogen absorption property of all samples under hydrogen atmosphere for different periods was investigated by thermo-gravimetric analysis, and results are shown in Figure 4. Some of the curves relating mass incorporation and time for the above temperatures were obtained. The data of hydrogen absorption and results are summarized in **Table 1**.

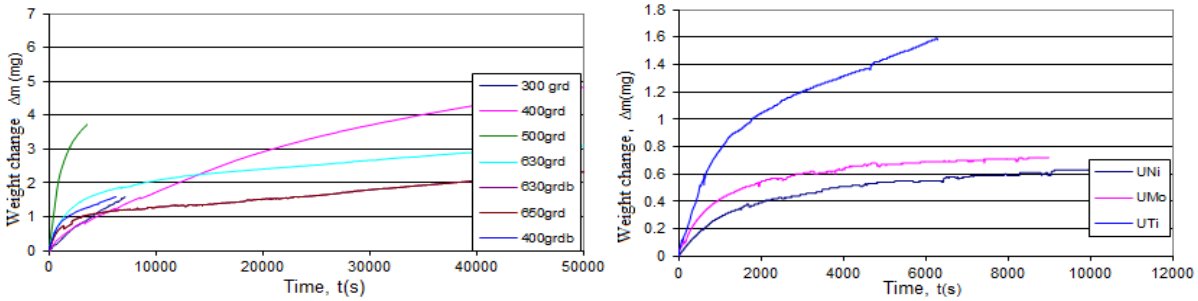

Figure 4 *The absorption curves for U-Ti samples, under isothermal conditions*

Table 1 *Data related to samples and measurements*

Sample	Sample weight (g)	Temp. (°C)	Time (h)	Conv. Factor α_{max}	a	b	R^2	Number of H atoms absorption
UTi-1	0.11626	300	2	0.80115	0.0005	0.8284	0.997	4
UTi-2	1.19823	400	2	0.09425	0.0024	0.4212	0.980	4
UTi-3	1.59491	400	70	0.24998	0.0003	0.5872	0.995	4
UTi-4	1.97888	500	1	0.13472	0.0017	0.5406	0.964	4
UTi-5	1.19823	630	20	0.20878	0.0087	0.2824	0.989	4
UTi-6	1.73083	630	28	0.12801	0.0008	0.4404	0.973	4
UTi-7	1.73083	650	70	0.25768	0.0001	0.5966	0.991	4
A comparison between experimental data for hydrogen absorption of U alloys								
UTi-2	1.19823	400	2	0.09425	0.0402	0.4212	0.980	4
UNi-1	0.39696	400	3	0.12145	0.0278	0.3426	0.965	4
UMo-1	0.61363	650	2.5	0.09795	0.0615	0.2769	0.934	4

The obtained hydrogen absorption kinetic curves were fitted using rate equations to reveal the mechanism of hydriding processes (as shown in **Figure 5**). Based on the absorption curves was determined the α conversion factor. The conversion factor α is given by following relation:

$$\alpha_{\max} = \frac{\Delta m}{m_x} \tag{1}$$

$$m_x = m * \left[\frac{M_H}{M_U + M_{AE}} \right] \tag{2}$$

Where m is sample weight and M_H, M_U and M_{AE} are atomic mass corresponding to hydrogen, uranium and alloying elements.

Table 2 *Values of m_x vs number of hydrogen atoms*

Number of H atoms	$M_H/(M_U+M_{Ti})$	Number of H atoms	$M_H/(M_U+M_{Mo})$	Number of H atoms	$M_H/(M_U+M_{Ni})$
1	0.0034973	1	0.0034973	1	0.0139910
2	0.0069545	2	0.0069545	2	0.0104930
3	0.0104930	3	0.0104930	3	0.0069545
4	0.0139910	4	0.0139910	4	0.0034973

Hydriding kinetics is given by the law:

$$y = a \cdot x^b \tag{3}$$

Where a and b are the coefficients of law fitted (see **Table 1**), y is the weight change and x is the time. According to data presented, the sample UTi-1 heated at 300°C, hydriding kinetics is described by almost linear law. For the samples heated between 400-700°C, hydriding kinetics is described by parabolic law, excepting of UTi-5 samples where hydriding kinetics is described by cubic law same as UMo -1 and UNi-1 samples.

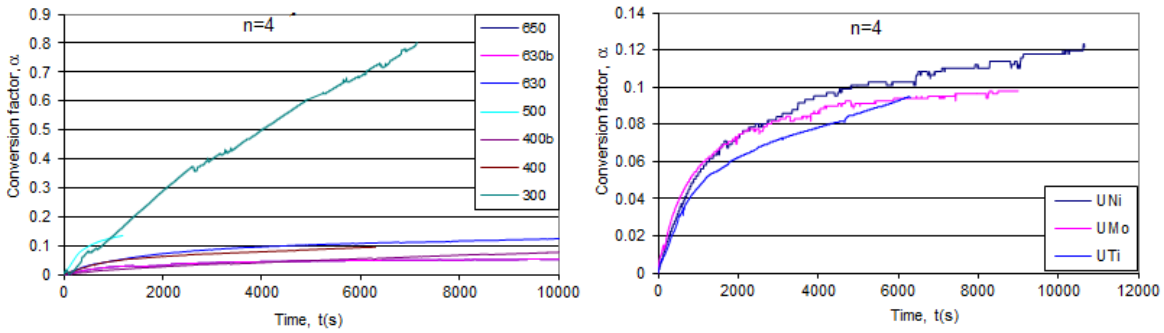

Figure 5 *Plots α_{max} vs time for U alloys at different temperatures*

Figure 6 shows observed phase in the X-diffraction patterns of hydrogenated specimens. X-ray diffraction proved that the specimens were not of a single phase but contain also and some transient phase, probably because of the inhomogeneity.

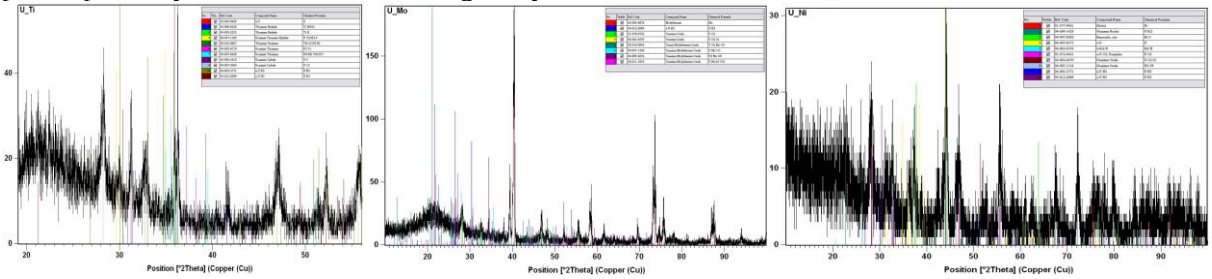

Figure 6 *X-ray diffraction patterns of hydrogenated samples*: *U-Ti (left), U-Mo (center), U-Ni (right)*

Conclusions

In order to improve the properties of uranium as hydrogen storage material, various uranium alloys were examined Preliminary examination on hydriding properties of uranium alloys exhibited that uranium alloys absorbs hydrogen at high capacity and promises them to be used for hydrogen storage materials. Further experiments should be continued.

References

[1] J. Smith, Trans. Intl. Conf. Research Reactor Fuel Management (RRFM'98), Bruges, Belgium, March 29-31, 1998, p. 99

[2] O.S. Ivanov, T.A. Badaeva, R.M. Sofronova, V.B. Kishenevskii, N.P. Kushnir, *Phase Diagrams of uranium Alloys*, TT 76-52046

[3] Bernhard Blumenthal, *The transformation temperatures of high-purity uranium*, Journal of Nuclear Materials, Volume 2, Issue 1, March 1960, Pages 23–30

[4] Robert D. Kolasinski, Andrew D. Shugard, Craig R. Tewell, and Donald F. Cowgill, Uranium for hydrogen storage applications: A materials science perspective

[5] V.P.Sinha, G.J.Prasad, P.V.Hegde, R.Keswani, C.B.Basak, S.Pal, G.P.Mishra, *Development, preparation and characterization of uranium molybdenum alloys for dispersion fuel application*, Journal of Allozs and Compounds 473 (2009) 238-244

[6] Takuya Yamamoto, Hideo Kayano and Michio Yamawaki, *New ternary Hydride Formation in U-Ti-H system*

[7] Oliveira FBV, Development *of a High Density Fuel Based on Uranium-Molybdenum Alloy with High Compatibility in High Temperatures*. PhD thesis, University of São Paulo, 2008

[8] S.C. Parida, Ram Avtar Jat, M.B. Rajan, S.G. Kulkarni and Ziley Singh Chaudhary, U-Ti alloy as a promising storage material for hydrogen isotopes