CHEMICAL ANALYSIS OF THE ELEMENTS IN UZrNb ALLOY AT CDTN: PRELIMINARY INVESTIGATION

Wilmar Barbosa Ferraz, ferrazw@cdtn.br
Helena Eugênia L. Palmieri, help@cdtn.br
Sérgio Carneiro dos Reis, reissc@cdtn.br
Ana Maria Matildes dos Santos, amms@cdtn.br
Adalberto Leles de Souza, adalbertoleles@yahoo.com.br

Centro de Desenvolvimento da Tecnologia Nuclear, CDTN–CNEN
Av. Presidente Antônio Carlos 6.627
31270-901 Belo Horizonte, MG-Brazil

Abstract. *The complete determination of major, minor, and impurity element contents in nuclear fuel is essential for quality assurance in the production of nuclear fuels. The control over all the stages of the development of nuclear fuel involves a combination of different analytical methods such as spectrometric methods. The goal of our investigation is to develop and evaluate procedures for the determination of main elements and carbon impuriy present in some uranium alloys. In this paper the element contents in U2.5Zr7.5Nb, U3Zr9Nb alloys and U6Nb, in weight percent, were investigated by means of scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS), inductively coupled plasma mass spectrometry (ICP-MS), wavelength dispersive fluorescence spectrometry (XRF/WDS) and energy-dispersive X-ray spectroscopy (EDX). The total carbon was determined using a carbon analyzer in which the sample is oxidized to carbon dioxide (IR absorption). It was observed a satisfactory correlation between the results obtained by employed methods.*

Keywords*: U-Zr-Nb, analytical methods, nuclear fuel*

1. INTRODUCTION

There have been worldwide efforts to replace highly enriched uranium fuels with low-enriched ones (≤ 20% 235U), mainly with the purpose of avoiding nuclear proliferation. To achieve this objective maintaining criticality and cycle length requirements, and trying to keep the same fuel configuration and the existing manufacturing technologies, it is necessary to develop high density uranium metallic fuels to compensate the reduction of enrichment [Burkes, Fielding and Porter,2009; IAEA, 2003].

To improve fuel performance in reactors, alloying elements of transition metals in groups V though VIII are added to uranium. These alloys have been investigated to the development of fuels in a dispersion and monolithic forms. Metals such as Zr, Nb and Mo allow the metastable γ phase retention for a long times at the relatively low fuel temperatures during the operation of research or test reactors [Ewh, Perez, Keiser and Sohn, 2010; Erickson, Jaynes, Sandstrom, Seegmiller and Taub, 1972].

Determination of the main elements and impurities in metallic fuel alloys consisting of uranium and alloying elements is of great importance in the development of these alloys from the point of view of its usefulness in nuclear fuel technology. These alloys with their main constituents and impurities can affect the mechanical performance of the fuel and can also influence the neutronics conditions in the reactor [Meyer et al. 2002].

There are several techniques for this determination that offer an impressive number of tools that allow the simultaneous determination of a large number of elements and compounds in very low concentration levels in a short time by using small amounts of sample. It is well known that the knowledge of important tools of elements analysis is fundamental to assure chemical quality of fuels materials.

There are some limitations for impurities analysis in U alloys as follows: low atomic number elements, e.g., Li, Be, B are difficult to be analyzed; uranium matrix has a high absorption coefficient for all analytic lines; U-X-ray spectrum is rather rich consisting many L and M lines, of first, second and third order of diffraction; in some cases scattered X-ray tube lines increase the possibility of spectral interferences, etc.

Centro de Desenvolvimento da Tecnologia Nuclear (CDTN) is developing the U-2.5Zr-7.5Nb and U-3Zr-9Nb (weight %) alloys by conventional melting process and by innovative process of sintering [5] as fundamental materials to the development of fuels in a dispersion and monolithic forms.

Under these aspects, CDTN is also developing and implementing some procedures of spectroscopic methods to support the development of plate-type dispersion nuclear fuel based on UZrNb alloys. Then, it was investigated methods as energy dispersive X-ray spectroscopy (SEM/EDS), inductively coupled plasma mass spectrometry (ICP-MS), wavelength dispersive fluorescence spectrometry (XRF/WDS) and energy dispersive X-ray (EDX). They should

be well known to be applied to a specific material under development. The total carbon was also determined using a carbon analyzer in which the sample is oxidized to carbon dioxide (IR absorption).

2. MATERIALS AND METHODS

Some analytical methodologies were used such as SEM/EDS, ICP-MS, XRF/WDS and EDX to determination of the main elements in U2.5Zr7.5Nb, U3Zr9Nb and U6Nb alloys developed at CDTN by conventional melting process in induction furnace with graphite crucible. It was also measured the carbon content using an elemental analyzer (equipment LECO) in which the sample is oxidized to carbon dioxide (IR absorption). The carbon is the principal impurity in these alloys that is introduced from graphite crucible used in the casting step. The carbon presence in these alloys can influence its microstructure in terms of carbides presence [Ewh, Perez, Keiser and Sohn, 2010]. As the analytical methodologies for the other impurities in uranium based alloys are still in development at CDTN they are not evaluated in this work.

Samples were prepared for analyses by spectroscopic methods as SEM (equipment JEOL, model JXA-8900RL) in conjunction with EDS (equipment Thermo Electron Corporation, model Noran System Six), XRF/WDS and EDX (equipment KEVEX, model Sigma-X 9050). Then, samples were cut using a diamond saw, mounted in a conductive resin, ground with SiC paper decreasing the abrasive grit from 220 to 2000, and then finally polished using diamond pastes of 3 and 1μm. It was taken an average of 10 measurements on different microscopic sections of sample.

For analysis by ICP-MS technique it was necessary to open the sample for the chemical separation of uranium. Samples of approximately 0.1 g were cut into three different positions in each type of alloy which was digested by means of a microwave system (Multiwave 3000, Anton Paar) using an acid mixture (HNO_3: HF: H_2O) in the ratio of 5:1:1. For the analysis of uranium, an excess of ferrous sulfate was used to reduce uranium (VI) in solution to uranium (IV) in phosphoric acid medium. The excess of iron (II) was selectively oxidized to Fe (III) with nitric acid in the presence of molybdenum (VI) as catalyst. After dilution with 1M sulfuric acid solution and the addition of vanadyl sulfate, uranium (IV) was titrated with potassium dichromate solution to a potentiometric end point [Ketterer, Scott and Szechenyi, 2008).

3. RESULTS AND DISCUSSION

Tables I to V show the contents of the main alloy elements obtained by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS), inductively coupled plasma mass spectrometry (ICP-MS), wavelength dispersive fluorescence spectrometry (XRF/WDS), energy-dispersive X-ray spectroscopy (EDX), and carbon content. In these tables are also shown the standard deviations (SD) of the measurements.

Table I – ICP-MS results.

Alloy	U (w/o)	Zr (w/o)	Nb (w/o)
U-2.5Zr-7.5Nb	88.68 (SD=0.08)	2.35 (SD=0.02)	9.11 (SD=0.11)
U-3Zr-9Nb	86.61 (SD =0.11)	2.49 (SD =0.02)	11.04 (SD =0.04)
U-6Nb	93.10 (SD=0.07)	-	6.79 (SD=0.04)

Table II – FRX results.

Alloy	U (w/o)	Zr (w/o)	Nb (w/o)
U-2.5Zr-7.5Nb	88.98 (SD=0.39)	2.58 (SD=0.02)	7.34 (SD=0.03)
U-3Zr-9Nb	88.47 (SD=0.40)	3.12 (SD=0.01)	8.91 (SD=0.04)
U-6Nb	92.73 (SD=0.21)	-	5.62 (SD=0.03)

Table III – SEM/EDS results.

Alloy	U (w/o)	Zr (w/o)	Nb (w/o)
U-2.5Zr-7.5Nb	89.97 (SD=0.61)	2.63 (SD =0.39)	7.40 (SD =0.27)
U-3Zr-9Nb	87.67 (SD =0.17)	2.62 (SD =0.21)	9.71 (SD =0.31)
U-6Nb	94.16 (SD =0.42)	-	5.88 (SD =0.42)

Table IV – EDX results.

Amostra	U (w/o)	Zr (w/o)	Nb (w/o)
U-2.5Zr-7.5Nb	89.7 (SD =0.25)	2.6 (SD =0.05)	7.8 (SD =0.25)
U-3Zr-9Nb	88.2 (SD =0.13)	2.9 (SD =0.09)	9.0 (SD =0.07)
U-6Nb	94.1 (SD =0.20)	-	5.9 (SD =0.17)

Table V – Carbon content.

Alloy	C (ppm)
U-2.5Zr-7.5Nb	625 (SD =2.62)
U-3Zr-9Nb	480 (SD =24.3)
U-6Nb	1341 (SD =74.9)

The values of the main elements in the U2.5Zr7.5Nb, U3Zr9Nb and U6Nb alloys were comparable when analyzed by different techniques (ICP, FRX, SEM/EDS and EDX). The standard deviations obtained by ICP-MS technique were lower than those obtained by other techniques. The evaluated carbon concentrations in these alloys were in the range of 480 to 1341 ppm which values are smaller than 2000 ppm that is the limit of design specification for uranium based alloys (Durazzo, Souza, Carvalho, Silva, Riella, 2011).

4. CONCLUSIONS

Different techniques for measurement of main elements of the U2.5Zr7.5Nb, U3Zr9Nb and U6Nb alloys were investigated. The obtained results employing the FRX, SEM/EDS, EDS and ICP-MS methods were comparable but the ICP-MS method shows lesser values in terms of standard deviations. The concentrations of carbon determined in these alloys were in the range 480-1341 ppm.

4. ACKNOWLEDGEMENTS

The authors are grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for the financial support.

5. REFERENCES

Burkes, D. E. and Fielding, R. S. and Porter, D. L., 2009. Metallic fast reactor fuel fabrication for the global nuclear energy partnership. Journal of Nuclear Materials, Vol.392, pp. 158–163.

Erickson, W.C. and Jaynes, G.E. and Sandstrom, D.J. and Seegmiller, R. and Taub, J.M., 1972. Evaluation of Uranium Alloys, Report LA-5002, Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

Ewh, A. and Perez, E. and Keiser, D.D. Jr. and Sohn, Y.H., 2010. Microstructural Characterization of UNb-Zr, U-Mo-Nb, and U-Mo-Ti Alloys via Electron Microscopy. Journal of Phase Equilibria and Diffusion, Vol. 31, No. 3.

IAEA-TECDOC-1374. 2003Development status of metallic, dispersion and non-oxide advanced and alternative fuels for power and research reactors.

Meyer, M.K. et al., 2002. Low temperature irradiation behavior of uranium–molybdenum alloy dispersion fuel. Journal of Nuclear Materials, Vol. 304, pp. 221.

Michael E. Ketterer, Scott C. Szechenyi. 2008. Determination of plutonium and other transuranic elements by inductively coupled plasma mass spectrometry: A historical perspective and new frontiers in the environmental sciences, Spectrochimica Acta Part B 63,pp 719-737.

6. RESPONSIBILITY NOTICE

The authors Adalberto Leles de Souza, Helena Eugênia L. Palmieri, Sérgio Carneiro dos Reis, Ana Maria Matildes dos Santos and Wilmar Barbosa Ferraz are the only responsible for the printed material included in this paper.