

ELECTRODEPOSITION OF URANIUM OVER NICKEL USING AQUEOUS ELECTROLYTE

Saliba-Silva, A.M.; Carvalho, E.F.U.; R. H. L. Garcia

Av. Prof. Lineu Prestes, 2242 – CEP: 05508-000 - São Paulo - SP - Brasil

saliba@ipen.br

IPEN - Instituto de Pesquisas Energéticas e Nucleares - São Paulo - SP

ABSTRACT

For radioisotope production, uranium must be properly processed and sealed before its irradiation inside the reactor pool. For this purpose, U-Al_x has been a common choice, due to its reduced neutron cross section and mechanical stability in reactor pool environment conditions. Nevertheless, at radioisotopes separation procedure, the chemical dissolution of aluminum comprises an alkaline route, what is a reduced yield process that generates large amounts of radioactive waste. Pursuing a better procedure, this work proposes an electrochemical deposit of uranium over nickel, which could be mechanically removed from an aluminum casing, avoiding the problems related to aluminum dissolution. In this sense, pulsed electrodepositions of nickel were run over aluminum substrates, followed by uranium electrodeposition, using aqueous electrolytes. Samples were characterized by alpha, gamma and beta counter, XRD and SEM. Although the electrodeposition of uranium still needs some progress, the results suggest a possible alternative route of uranium target production.

Keywords: electrodeposition, nickel, uranium.

INTRODUCTION

Tecnecium-99 metastable (^{99m}Tc) is the most common pharmaceutical, used in many diagnostics, including thyroid, bones and breast cancer. This radioisotope

can be generated from the decay of Molybdenum-99 (^{99}Mo), which is a subproduct of ^{235}U fission. The manufacture process of ^{99}Mo comprises neutron irradiation of ^{235}U in a nuclear reactor. About 45kg of HEU (Highly Enriched Uranium) is used annually for the production of medical isotopes, and there is an effort for substituting the currently used producing method for LEU (Low Enriched Uranium) - based production routes, in accordance with the RERTR program ^(1,2).

For its use in the new Brazilian Multipurpose Research Reactor (*Reator Multipropósito Brasileiro – RMB*), LEU targets with 2g of ^{235}U (or 10g of total uranium) are being developed. The most advanced design so far at IPEN is based on U-Al(x) dispersion on an aluminum matrix. However, at post-irradiation chemical separation of radioisotopes, this design comprehends an alkaline dissolution route, what implies on considerable losses of ^{99}Mo , and large quantities of liquid radioactive material as waste ^(3,4).

A design based on the substitution of aluminum by nickel is a promising alternative, since nickel fulfills the neutronic, mechanical and chemical requirements at the corrosive reactor pool environment. The later extraction of radioisotopes from nickel/uranium is done via an acid route, which permits better yields and lower volumes of waste. Additionally, nickel dissolves 8 times faster than uranium ⁽⁴⁾. Some uranium target designs include a thin foil of uranium comprised between nickel, but the rolling processes related to this route are difficult and expensive ⁽³⁾.

The information before mentioned, together with the development of electrochemical processes of uranium and nickel depositing techniques, makes the study of different uranium targets designs notably attractive. Among these possibilities, an uranium target based on the electrodeposition of uranium comprised between electrodeposited nickel. Besides the simple and cheap processing involved with electrodeposition techniques, nickel permits a better adhesion of uranium than aluminum ⁽⁵⁾.

Electrodeposition is a process for depositing a coating by means of electrolysis. It comprises, basically, an electrical source, electrodes and an electrolyte (bath).

To deposit nickel, the Watts bath, an aqueous electrolyte, is a well established method to deposit this metal. A Watts bath can be reasonably well represented by nickel sulfate (240 to 340g/l), nickel chloride (30 to 60g/l) and boric acid (30 to 40g/l). Still, this system allows a fine tune of the final microstructure if pulsed electrodeposition methods are used. It consists basically in shutting down and turning

on the deposition current in high frequencies. Moreover, sodium lauryl sulphate can be added in low concentrations to reduce the adhesion of hydrogen bubbles on the cathode, avoiding imperfections on the final deposit ^(6,7).

In uranium deposition, ionic liquids and solvents as *n,n*-dimethylformamide, tetrabutylammonium hexafluorophosphate and isopropanol are commonly used. In these kinds of baths, high current are required in order to surpass the baths low conductivity. To avoid these conditions, aqueous baths based on saturated ammonium chloride can be used, although uranyl nitrate can also be used ^(8,9,10). Concerning these data, the present study aims to develop a uranium target using electrodeposited uranium over previously electrodeposited nickel ^(11,12,13).

MATERIALS AND METHODS

An Autolab 302N potentiostat/galvanostat equipped with a high frequency module ADC 10M was used for the electrodeposition procedures, at ambient temperature. The system cell consists in a fixed cathode on the bottom, tight with a o-ring and a bath volume around 35mL. For nickel depositions, aluminum 6061 was used as a substrate and previously cleaned. In these cases, Watts bath with sodium lauryl sulphate was used and the pH was controlled with concentrated sulfuric acid around 2.5. The applied current was 19mA/cm², with a duty cycle of 50% of 0.05s pulses, with a total deposition time of 1h23m. The used anode was metallic nickel, and a Ag/AgCl/KCl (sat.) was used as standard electrode (+0.205 mV SHE). The system was kept stirring under 500 RPM. For uranium depositions, platinum was used as anode, and aqueous solutions of uranyl nitrate used as electrolyte. The conditions of uranium depositions are described in table 1. In these cases, one minute before the end of the deposition current, 10mL of NH₄OH 3M was added to fix the deposit, assuring a final pH around 9. A Hitachi TM3000 scanning electron microscope (SEM) with a Bruker Quantax 70 EDS system module was used to obtain images and elementary data of the microstructure. All the images were obtained using backscattered electrons. X-ray diffraction data (XRD) were acquired in a Rigaku Multiflex using Cu- α radiation. Reference diffraction peaks were extracted from ICDD (International Crystallography Diffraction Data) files. For quantification of the uranium deposited, a reference graph of beta and gamma counts was plotted using known quantities of uranyl nitrate with a Ludlum 2929 Dual Scaler Counter.

Table 1. Uranium electrodeposition conditions

Sample	Electrolyte concentration (M)	pH	Current (mA)	Deposition time (h)
UND-1	0.0003	2.8	-8	0.5
UND-2	0.0003	2.8	-1	1
UND-3	0.0003	2.8	-1	3
UND-4	0.0003	2.8	-1	0.4
UND-5	0.05	1.5	-1	1
UND-6	0.05	1.5	-1	12
UND-7	0.05	1.5	-10	1
UND-8	0.05	1.5	-100	1
UND-9	0.05	1.5	-10	12
UND-10	0.05	1.5	-1000	0.05

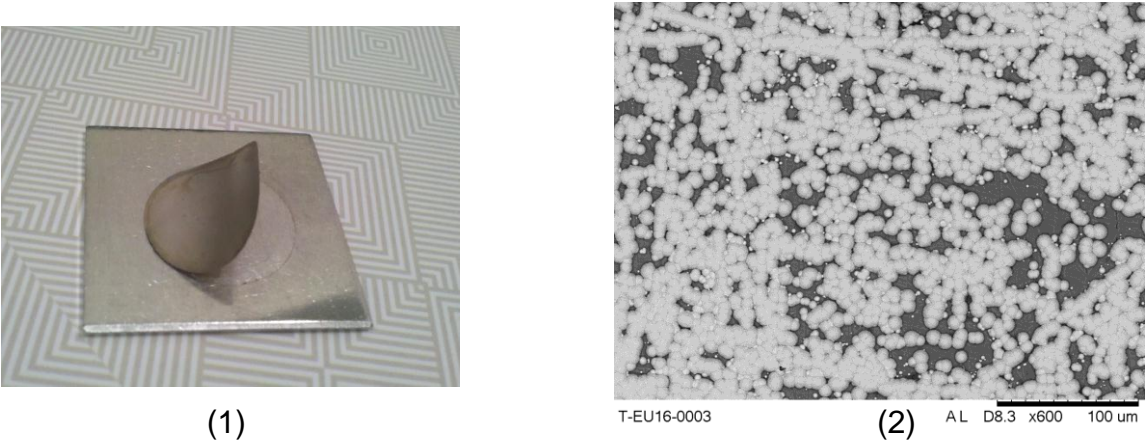
RESULTS AND DISCUSSION

Aluminum substrate cleaning: We tested water with soap, ethanol and acetone, ultrasonic cleaning, sandpaper abrasion, chemical attack with potassium hydroxide and hydrochloric and nitric acid. The most successful results concerning aluminum cleaning for electrodeposition were achieved with concentrated hydrochloric acid. The failure of the other methods can be attributed to the inability of removing the superficial oxide layer, or, in the case of potassium hydroxide, the formation of a sticky gel that could not be removed in subsequent washings. Examples of poor adhesion and heterogeneous deposition (due to insufficient cleaning or oxide removal) are shown at fig.1 and 2.

Nickel electrodeposition: As mentioned before, nickel deposition was carried out with pulsed current, making possible to minimize the grain size and maximize the leveling of the surface, avoiding the use of other additives. The current value used was tested as the maximum before producing “burned” the deposit. It can be said that the electrodeposition speed was considerably fast, producing a smooth and resistant deposit in less than two hours. A SEM of the surface is shown at figure 3. At X-ray diffraction, the nickel deposit shows crystalline and pure (fig. 4).

Uranium electrodeposition: Although relatively uniform, uranium deposits over nickel shows high frequencies of cracks and low-adhesion areas (fig. 5). The EDS analysis confirmed uranium presence in composition (fig.6). Since the uncertain quantity of hydroxide contained in deposits, uranium amount cannot be established by mass. In this sense, we plotted a calibration curve using α and $\beta+\gamma$ counts, with

known quantities of uranyl nitrate and correlated with different experiments. These results are shown in table 2.



Figures 1 and 2: (1) electrodeposited nickel bad adhered over aluminum due to insufficient substrate cleaning, with acetone. (2): SEM of a heterogeneous nickel deposit over aluminum, previously cleaned with ethanol

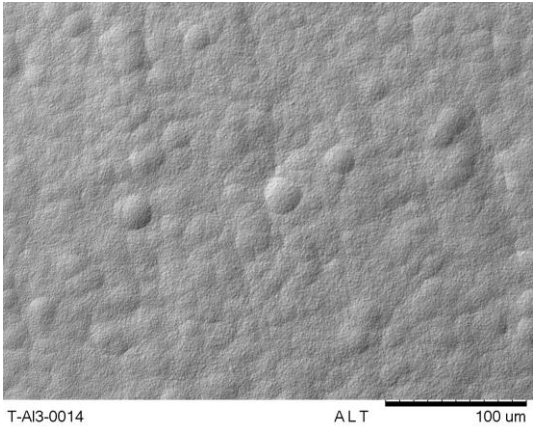


Figure 3: Nickel electrodeposited over aluminum on an adequately clean surface

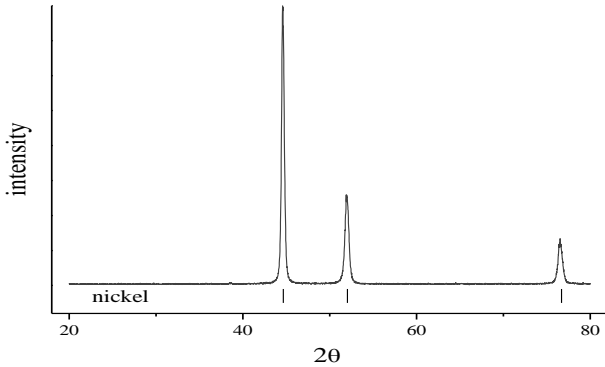


Figure 4: XRD data from electrodeposited nickel

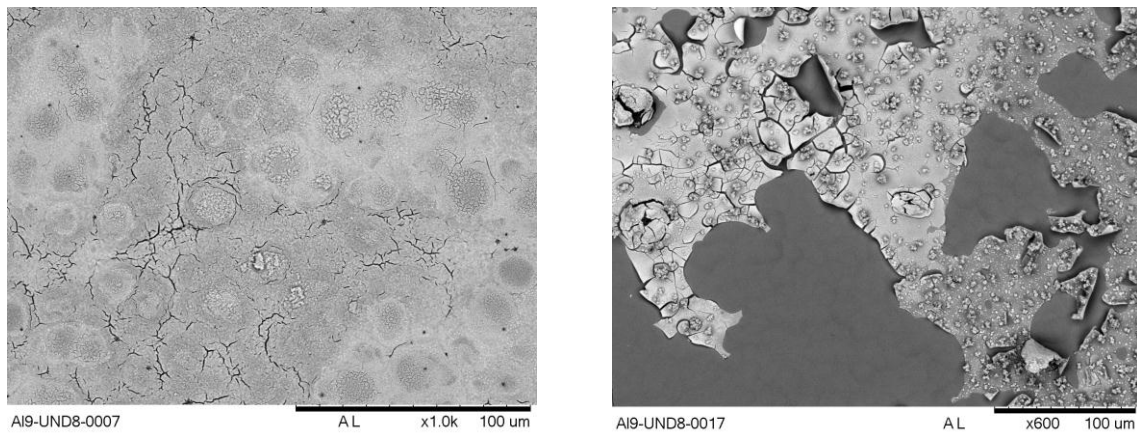


Figure 5: SEM of uranium electrodeposited over nickel

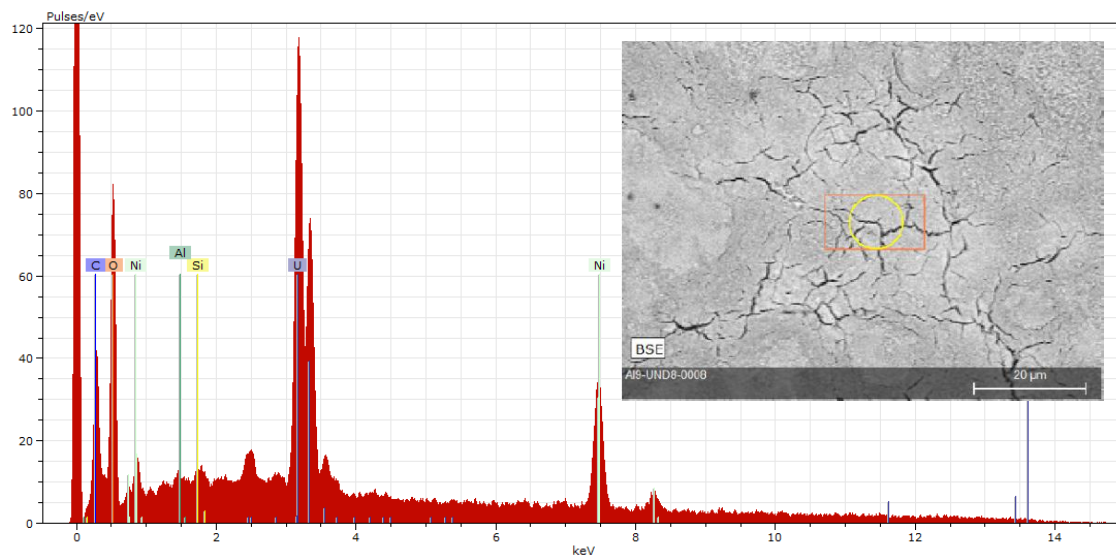


Figure 6: SEM and EDS analysis of uranium electrodeposited over nickel

Table 2: Uranium electrodeposition parameters and mass/counts correlation

Sample	Electrolyte concentration (M)	Current (mA)	Deposition time (h)	Alfa (counts/20 min)	Beta+gamma (counts/20 min)	U mass (g) (α correlation)	U mass (g) ($\beta\gamma$ correlation)
UND-1	0.0003	-8	0.5	160	2101	0.0155	0.0001
UND-2	0.0003	-1	1	260	2320	0.0286	0.0001
UND-3	0.0003	-1	3	4073	6159	0.5271	0.0017
UND-4	0.0003	-1	0.4	645	2875	0.0789	0.0004
UND-5	0.05	-1	1	327	2317	0.0373	0.0001
UND-6	0.05	-1	12	322	2289	0.0367	0.0001
UND-7	0.05	-10	1	1064	3437	0.1337	0.0006
UND-8	0.05	-100	1	3457	9459	0.4465	0.0031
UND-9	0.05	-10	12	2962	6872	0.3818	0.0020
UND-10	0.05	-1000	0.05	531	2344	0.0640	0.0002

There is some discrepancy in quantification in respect with the radiation used. It seems that current is a more important parameter than time, in terms of amount of uranium deposited.

CONCLUSION

Electrodeposition of nickel over aluminum substrates using pulsed techniques is a convenient technique to control the microstructure of the final deposit. The cleaning of aluminum substrate is a very important step for deposit adhesion, and the best results were achieved with concentrated hydrochloric acid. Uranium electrodeposition using uranyl nitrate as electrolyte was successful, but the results indicate that further development should be made in order to obtain dense and adhered deposits. Quantification technique of deposited uranium by α counts seems to have better agreement than $\beta+\gamma$ counts.

ACKNOWLEDGEMENTS

The authors thank the CCN – Nuclear Fuel Centre of IPEN, and the FAPESP support, via project 2010/01244-2.

REFERENCES

1. National Research Council Committee: ***Medical isotope production without highly enriched uranium***. ISBN:0-309-13040-9, National Academies Press. 2009.
2. Argonne National Laboratory. ***Reduced Enrichment for Research and Test Reactors (RERTR) Program***. Information on <http://www.rertr.anl.gov/>, accessed on oct/2011.
3. DOMINGOS, D. B.; SILVA, A. T. E.; SILVA, J. E. R. DA; JOÃO, T. G. Neutronic Analysis for Production of Fission Molybdenum-99 at IEA-R1 e RMB Research Reactors. In: EUROPEAN RESEARCH REACTOR CONFERENCE, Rome, Italy, 2011. ***Proceedings***... Rome, Italy: 2011.
4. LEONARD, R. A.; CHEN, L.; MERTZ, C. J.; VANDEGRIFT, G. F. Progress in dissolving modified LEU cintichem targets. In: INTERNATIONAL MEETING ON REDUCED ENRICHMENT FOR RESEARCH AND TEST REACTORS, Seoul, Korea, 1996. ***Proceedings***... Seoul, Korea: 1996.

5. MCAULIFFE, CLAYTON. **Quantitative electroplating of uranium for isotopic analysis using nickel and monel as base metals**. Clinton Engineering Works, 1946.
- 6 . WATTS, O. P. Rapid Nickel Plating. **Transactions of the American Electrochemical Society**, v. 29, p. 395–403, 1916.
7. MANDICH, N. V.; GEDULD, H. Understanding and troubleshooting decorative nickel electroplating systems—part I: Introduction and brightness problems. **Metal Finishing**, v. 100, n. 2, p. 83–91, 2002.
8. ALENCAR, M. M.. **Determinação de isótopos de urânio e tório em amostras de líquens canoparmelia texana**. Dissertação – Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN, São Paulo - SP, 2011.
- 9 . DONNAN, M. Y.; DUKES, E. K. Carrier Technique for Quantitative Electrodeposition of Actinides. **Anal. Chem.**, v. 36, n. 2, p. 392–394, 1964.
10. DA CRUZ, P. A. L.; POLEDNA, R. Alpha-source preparation by electrodeposition. **Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment**, v. 286, n. 3, p. 453–456, 1990.
11. KIM, W.; WEIL, R. Pulse plating effects in nickel electrodeposition. **Surface and Coatings Technology**, v. 38, n. 3, p. 289–298, 1989.
12. SALIBA-SILVA, A.M.; GARCIA, R.H.L.; MARTINS, I.C.; URANO DE CARVALHO, E.F.; DURAZZO, M. Nickel electrodeposition over powder compact for irradiation target. In: Eight International Latin-American Conference on Powder Technology, 06-09 November, 2011, Florianópolis, SC – Brazil. **Proceedings of the Eight International Latin-American Conference on Powder Technology**, 2011.
13. SALIBA-SILVA, A.M.; GARCIA, R.H.L.; MARTINS, I.C.; URANO DE CARVALHO, E.F.; DURAZZO, M. . Uranium Briquettes For Irradiation Target. In: 2011 International Nuclear Atlantic Conference, 24-28 October, 2011, Belo Horizonte, MG - Brazil. **Proceedings of the INAC 2011**, 2011.