

## Nickel electrodeposition over powder compact for irradiation target

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**Abstract.** Irradiation targets with 20% of  $^{235}\text{U}$  (Low Enriched Uranium - LEU) have been studied for replace HEU (Highly Enriched Uranium) targets in future nuclear reactors. These are used to produce the pair of radionuclides  $^{99}\text{Mo}$  /  $^{99\text{m}}\text{Tc}$ , used for diagnostics in nuclear medicine. This work aims to develop an alternative route to produce LEU targets. It consists in hydrogenating and powdering metallic uranium and compacting the produced powder, followed by sealing it with nickel by electrodeposition. The deposited nickel should suppress the release of fission gases, and avoid a reactive contact of uranium with aluminum from the enclosure. In order to obtain the best conditions for deposition over uranium, in this work, iron powder was compacted into small discs, with a diameter of 22 mm and weight of 14g, simulating an equivalent volume of 10g of LEU uranium powder. As well, aluminum discs were used to ensure adhesion and uniformity of the nickel layer. Pulsed nickel electrodeposition was carried out over the compacts, employing current frequency of 900Hz,  $-0.84\text{A}/\text{cm}^2$  of peak current and duty cycle of 0.5 in Watts Bath. The resistance of pulse Ni-plated layer was checked by experiments with impedance spectroscopy in plated samples using aluminum substrate, held in KCl (pH=6) giving EIS results after resting the discs in solution for 0h, 4h and 24h resting. The physical strength was evaluated qualitatively by treating the Ni covered compact at  $600^\circ\text{C}$ , developing a bump deformation on the original planar layer, up to the point to open the Ni-layer for gas relief. These results suggest an adequate mechanical strength of the Ni-layer for using under neutronic irradiation, sealing the radioactive gases, mainly  $^{140}\text{Xe}$ , produced during fission of  $^{235}\text{U}$ .

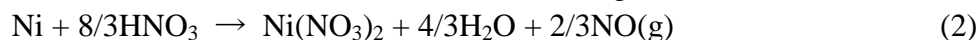
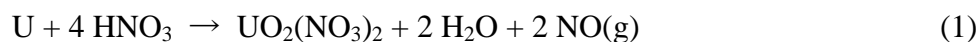
**Introduction.** The most common radiopharmaceutical is the technetium-99 metastable ( $^{99\text{m}}\text{Tc}$ ), which is used in many diagnostics, including thyroid, bones and breast cancer. This radioisotope is daughter from the decay of Molybdenum-99 ( $^{99}\text{Mo}$ ), which is fission subproduct of  $^{235}\text{U}$  fission. As many isotopes, the  $^{99}\text{Mo}$  is usually produced by neutron irradiation of  $^{235}\text{U}$  in a nuclear reactor. The irradiation target is shielded and placed in the reactor pool during 7 days to promote the maximum concentration of  $^{99}\text{Mo}$  for later extraction. Presently, about 45kg of HEU is used annually for the production of medical isotopes, and there is a lot of effort to develop LEU targets in accordance with the RERTR program [1,2].

IPEN has started recently developing a LEU irradiation target, based on dispersion matrix  $\text{UAl}_x$  alloy. The preliminary neutronic calculations revealed that the amount of uranium that will be placed in the core of this dispersion is 2.0 g of  $^{235}\text{U}$ , or about 10g total uranium. The uranium density is planned to be about  $2.8\text{-}2.9\text{ g}^{\text{LEU}}\text{U}/\text{cm}^3$ . This value may be used as a reference for assembly another designed core target. This density can produce under neutronic irradiation about 60 Ci/assembly according to Domingos et al [3].

Nevertheless, there is another research route of producing U targets, based on of U-Ni thin foil, which follows the post irradiation acid dissolution. However, there are irradiation tests showing problems related to welding U-foil with Ni-foil [4].

A fundamental difference between these target development routes is the post-irradiation treatment, since the aluminum dissolution is alkaline and the nickel one is acid. The alkaline dissolution route generates considerable losses of  $^{99}\text{Mo}$  incorporated with solid waste, and produces large quantities of liquid radioactive material as waste. However, the acid route for post-processing

U/Ni foil targets generates better yields and lower volumes of waste. It also should facilitate the handling during post-processing to separate the  $^{99}\text{Mo}$ , since the amount of Ni to be separated from uranium is relatively small, and nickel dissolves 8 times faster than uranium, as indicated Leonard et al [5]. As a disadvantage, this route makes it necessary to treat nitrogen oxides in gaseous form [1]. The route of acid dissolution follows the reactions (1) and (2):



Electrodeposition is a process for depositing a coating by means of electrolysis. It comprises, basically, an electrical source, electrodes and an electrolyte (bath). In the field of industrial nickel electrodeposition, the Watts bath, an aqueous electrolyte, has been used for almost one hundred years [6], and it is a well established method to deposit this metal. A Watts bath can be reasonably well represented by Nickel sulfate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ): 240 to 340g/l, Nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ): 30 to 60g/l and Boric Acid ( $\text{H}_3\text{BO}_3$ ): 30 to 40g/l.

Modernly, the electroplating technology has added wetting and brightener additives, such as sodium lauryl sulfate, sulfonamides, coumarin and many other organic compounds to this bath. The wetting agents are used to reduce the surface tension of the solution, avoiding the negative effect of hydrogen bubbles that are produced during the deposition process on the cathode. Thus, the hydrogen formation is not avoided, but the bubbles are released before it could locally inhibit the deposition. Moreover, brighteners added have the effect of inhibit the grain growth of nickel, and promote leveling and smoothness of the deposit [7,8].

However, for its utilization as casing of uranium targets, the deposited nickel should have the lowest possible contamination, in order to avoid the formation of sub products that could, eventually, be released during the irradiation process and unease the post-irradiation refining process. In this sense, the use of pulse electrodeposition could be a possible route, producing dense and smooth deposits without or with reduced amount of additives [9,10,11].

When compared to direct deposition methods, the pulsed electrodeposition offers better control over various microstructural parameters of the deposit. For example, the grain refinement adjust provides that more nucleation sites are formed during crystallization, detrimental of growth of existing nucleus. Its end effects are less porosity, higher shine and density, and better mechanical properties [9,11]. An important parameter is the duty cycle, described as the on-time divided by the sum of on and off-time [11].

The duration of these intervals are fundamental for the determination of the final characteristics of the deposit. Frequently, a duty cycle of 50% is used for Watts Bath system, and lower values for to obtain nanocrystalline nickel [10,12]. The peak current density ( $i_p$ ), is the value of current during the on-time. It is worth saying that, even though pulsed deposition makes possible to work with higher currents, limits has to be established, in order to avoid burned nickel deposits, which are dark and powdery deposits that occurs when excessive current is applied, due to its high nucleation rate, local raise of pH and water inclusion in the deposit [13,14].

Having these parameters defined, it is possible to determine the average current density ( $i_a$ ), that is the peak current times the duty cycle. This value represents a correlation to a value of current of direct deposition.

It is worth to mention that the average current density represents a rough calculation of the deposition speed; the microstructural characteristics of the deposit will be significantly different from one sample to another.

In addition, due to different electrodepositing conditions, distinct morphological phases can be obtained. Pure nickel,  $\alpha$ -nickel (a solid solution of Ni with small amount of H) and  $\beta$ -nickel (solid solution of Ni and H with more than 60% of H) [15].

Based on these data, the present study aims to develop a uranium target from metallic

uranium powder compact, covered with nickel pulse-electrodeposited, inside an aluminum case. The nickel layer must seal the uranium and avoid the leakage the radioactive gases, formed during irradiation process.

**Experimental procedure.** Iron powder, weighting 4.1g, with medium particle size of 325 $\mu\text{m}$ , was compacted into pellets of 22mm in diameter by uniaxial pressing at 260 Mpa. It resulted in 2.0mm-thick compacts with a total area of 8.98cm<sup>2</sup>. These pellets, as well samples of aluminum (AA1050) were subjected to Ni electrodeposition pulsing process. Watt's bath was used as electrolyte (0.85 mol.L<sup>-1</sup> NiSO<sub>4</sub>.6H<sub>2</sub>O + 0.15 mol.L<sup>-1</sup> NiCl<sub>2</sub> + 36 g.L<sup>-1</sup> H<sub>3</sub>BO<sub>3</sub>) lying the pH around 3. The material was submitted from 2 to 10 repetitions of pulse electroplating at 900 Hz, using a duty cycle of 0.5, what resulted in a "on time" of 10<sup>-3</sup>s and "off time" of 10<sup>-3</sup>s. The peak current used was 200 mA/cm<sup>2</sup>. Each pellet had a total deposition time around 1 to 8 min.

In order to evaluate the chemical resistance of nickel electrodeposited layer, electrochemical impedance spectroscopy experiments were carried out in a 3.5% KCl aqueous solution with pH=6. For electrochemical comparisons, plating substracts of a foil of pure nickel and AA1050 aluminum were also used. For these experiments, samples were immersed till the dE/dt variations were less than 10  $\mu\text{V/s}$ .

A potentiostat Metrohm Autolab 302N with frequency response analyzer (FRA) was used to perform the pulse electroplating and also to evaluate cyclovoltametric curves, corrosion rate and electrochemical impedance spectroscopy (EIS) studies. The counter electrode for FRA tests was a bar of AISI 310. For Ni-electroplating it was used electrolytic nickel bars. Counter-electrode areas were big enough to guarantee a proper polarization of working electrode. The reference electrode used was a standard Ag/AgCl/KCl (sat.) (+0.205 mV SHE). The FRA frequency spectrum was 10<sup>4</sup> to 10<sup>-2</sup> Hz.

To test the deformation resistance of the Ni-electrodeposited layer from gas formation inside the briquette, simulating the generation of <sup>140</sup>Xe during irradiation, a briquette containing sealed zinc stearate and water was subjected to 550°C during 5 hours.

**Results.** The Ni-electrodeposited Fe compacts exhibit homogeneous and dense covering of nickel. The aspect of the samples can be seen at figure 1a. Moreover, from a cut sample (figure 1b), it is possible to observe that there was a penetration of metallic nickel inside the iron compact structure. It represents more adhesion, density and homogeneity of the deposit. The technique of pulse electroplating was successful in terms of avoiding the grain growth and rough deposits, comparing to direct pulse methods.

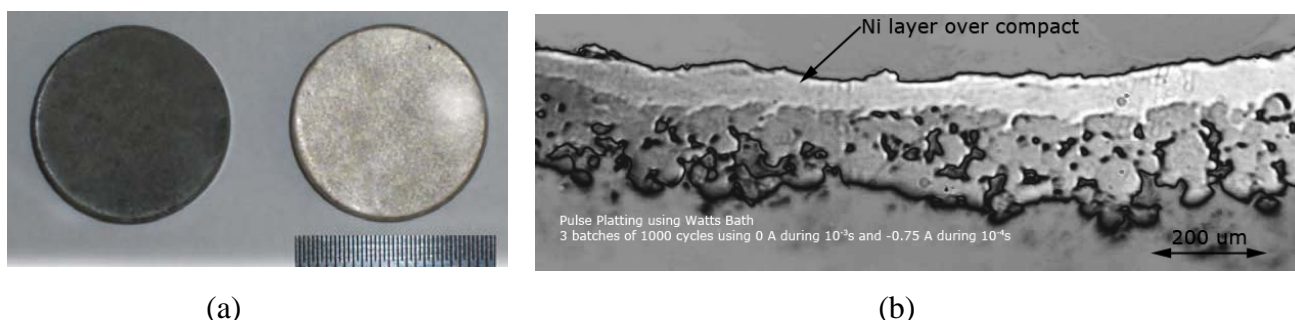


Figure 1 – (a) Iron-compact before and after the pulsing Ni-electrodepositing; (b) Micrography of the cut surface showing the appearance of nickel layer obtained by pulse electroplating.

Figure 2 shows an image from optical microscopy, of a cut sample that was subjected to 550°C during 5 hours, after the nickel deposition. Due the fact that it contained water and zinc stearate inside the pellet, the thermal treatment stretched nickel layer during, till the gases could be released. It suggests that this structure would have enough strength to seal nuclear gases generated during the irradiation process in the reactor pool.

Figure 3 shows a X-ray diffraction, from a layer of electrodeposited nickel, removed from the substract. It is possible to confirm the cristallinity of the Ni phase formed. The reference peaks were calculated from theoretical values.

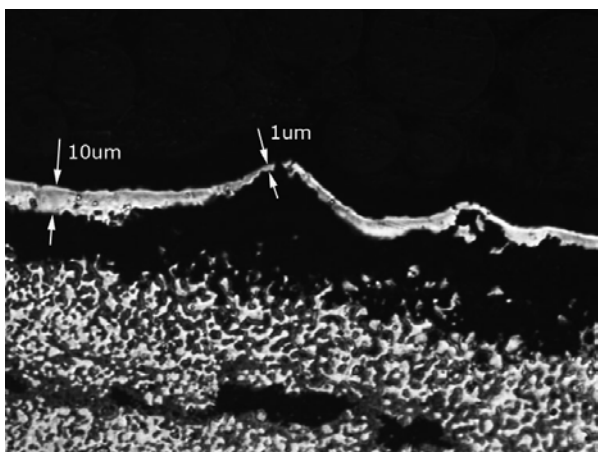


Figure 2 – Qualitative evaluation of Ni-layer after simulation of gas formation inside the plated briquette.

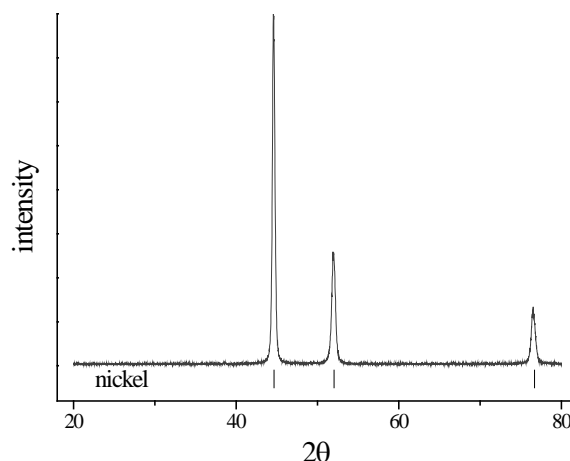


Figure 3 – X-ray diffractogram of the deposited nickel

In order to evaluate the chemical resistance of the nickel layer, initially, it was determined the corrosion potential of pure nickel as around -130mV, in KCl solution (figure 4). Nevertheless, in chloride solutions, the thin layer of electrodeposited nickel over aluminum tends to show corrosion potential more negative, around -500 to -600mV.

To have a fair comparison for the electroplating samples, the aluminum substract was slightly anodized, forming an imperfect structure of oxide with porosities. After electroplating, the pores in this structure became fulfilled and more conductive, diminishing the corresponding capacitive impedance of the metallic plated layer. The corrosion potential confirms this trend, indicated by evolution towards nobler potentials and becoming less prone to be corroded. These data suggests that the layer turned more chemically resistant (figure 5).

As can be seen from the Nyquist graphs of the electroplated material (Figure 8), the semicircles are apparent. It leads to the conclusion that a pure double layer condition has been formed over the deposited nickel inside the pores of anodized layer. This reduces the overall impedance of the structure, showed by the shrinking of the semicircles, as it becomes more plated by nickel. There is a progressive increase of the metallic nickel with the pulse plating cycles, leading to a full coverage of the anodized aluminum pores. The limit resistance decreasing would be the pure nickel coverage as shown in the graph. However, for the anodized layer over the Al-sample, this resistance reduction would not reach this level.

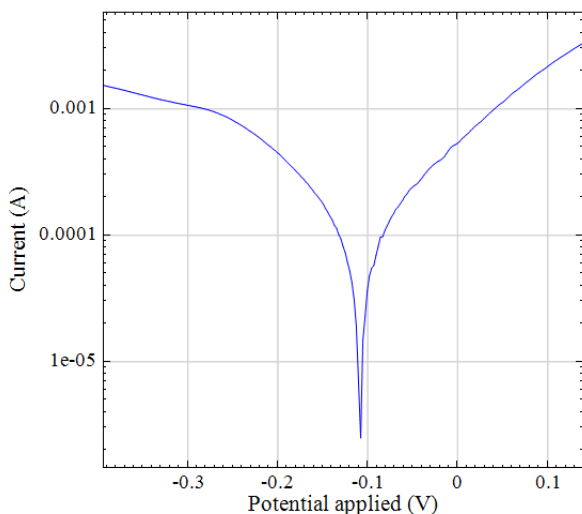


Figure 4 - Pure nickel corrosion potential evaluation around -108mV in 3.5%wt KCl solution.

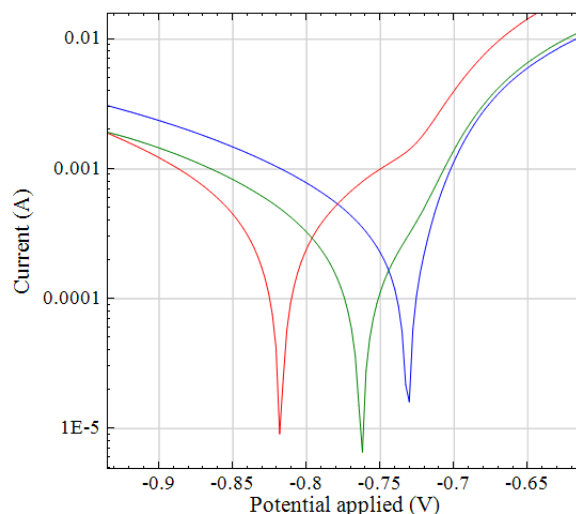


Figure 5 - Corrosion potential indications: [Red] Anodized aluminum; [Green] 2 cycles of Ni plating; [Blue] 10 cycles of Ni plating in Watt's solution.

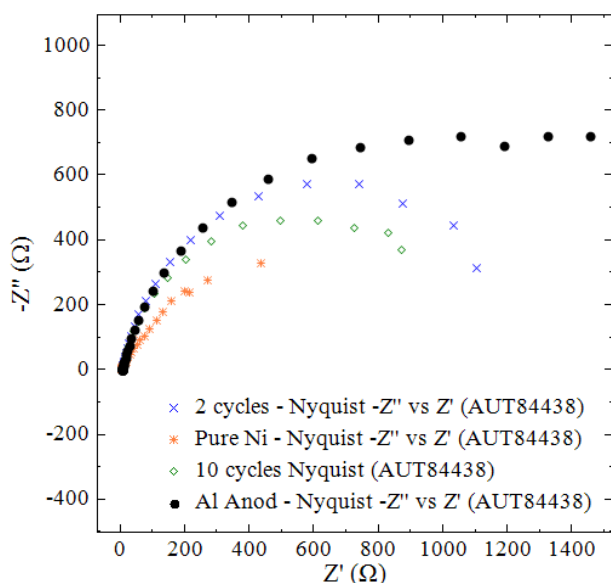


Figure 8. Nyquist diagram showing the evolution of the electroplating over anodized AA1050. (●) Anodized aluminum; (x) 2 cycles of pulse Ni-electroplating; (◇) 10 cycles of pulse Ni-electroplating; (\*) Pure Nickel.

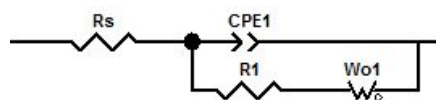


Figure 9. Proposed equivalent circuit model of studied system.  $R_s$  is the electrolyte resistance, CPE1 is the constant phase element, R1 is the charge transfer resistance and open Warburg component.

**Conclusion.** The pulsed technique is an adequate route for electrodepositing nickel over iron and aluminum, with reduced roughness, good homogeneity, mechanical properties, adhesion and cristallinity. The results obtained from the deposited layer, made from pure nickel, suggested that it would have sufficient mechanical strength to seal gases from nuclear fission, in case of its utilization over uranium in irradiation targets.

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