

URANIUM BRIQUETTES FOR IRRADIATION TARGET

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ABSTRACT

Direct irradiation on targets inside nuclear research or multiple purpose reactors is a common route to produce ⁹⁹Mo-^{99m}Tc radioisotopes. Nevertheless, since the imposed limits to use LEU uranium to prevent nuclear armament production, the amount of uranium loaded in target meats has physically increased and new processes have been proposed for production. Routes using metallic uranium thin film and UAl_x dispersion have been used for this purpose. Both routes have their own issues, either by bringing difficulties to disassemble the aluminum case inside hot cells or by generating great amount of alkaline radioactive liquid rejects. A potential route might be the dispersion of powders of LEU metallic uranium and nickel, which are pressed as a blend inside a die and followed by pulse electroplating of nickel. The electroplating provides more strength to the briquettes and creates a barrier for gas evolution during neutronic disintegration of ²³⁵U. A target briquette plated with nickel encapsulated in an aluminum case to be irradiated may be an alternative possibility to replace other proposed targets. This work uses pulse Ni-electroplating over iron powder briquette to simulate the covering of uranium by nickel. The following parameters were applied 10 times for each sample: 900Hz, -0.84A/cm² with duty cycle of 0.1 in Watt's Bath. It also presented the optical microscopy analysis of plated microstructure section.

1. INTRODUCTION

The technetium-99 metastable (^{99m}Tc) is the most common radiopharmaceutical, and it is used in many diagnostics, including thyroid, bones and breast cancer. It is formed by decay of Molybdenum-99 (⁹⁹Mo), a subproduct of ²³⁵U fission. This radioisotope is distributed weekly to hospitals inside generators that contain ⁹⁹Mo, since the ⁹⁹Mo has a half-life of 66 hours, and the ⁹⁹Tc has a half-life of 6 hours. As many isotopes, the ⁹⁹Mo is usually produced by neutron irradiation of ²³⁵U in a nuclear reactor. After the shielding and conformation of enriched uranium, it is placed in a reactor pool, for a relatively small period of 7 days to promote the maximum concentration of ⁹⁹Mo for later extraction. In most cases, the uranium target is made with HEU (Highly Enriched Uranium, having more than 20% wt of ²³⁵U) (1).

As HEU is still used today for production of ⁹⁹Mo, it is also produced for nuclear weapons. The amount of highly enriched uranium needed to achieve a chain reaction (critical mass) depends on high enrichment of the isotope ²³⁵U. So, there is concern about the possibility of fabricating nuclear explosive device. The critical limit to safe use of uranium is up to 20wt% enrichment of ²³⁵U, called LEU. Due to these problems of possible use of HEU for military purposes, it has been developed the RERTR program of the U.S. Department of Energy, since 1978, aiming at

reducing the enrichment of uranium to LEU for use in nuclear fuel and irradiation targets for production of ^{99}Mo (1). However, presently, about 40 to 50kg of highly enriched uranium is used annually for the production of medical isotopes (2). Currently, there is a lot of effort to develop LEU targets in accordance with the RERTR program (1).

IPEN has started recently developing a LEU irradiation target, in the same profile as the Argentinean production of ^{99}Mo - $^{99\text{m}}\text{Tc}$, which is based on dispersion matrix UAl_x alloy of aluminum. This type of target is fabricated according to picture frame technique outlined in Figure 1.

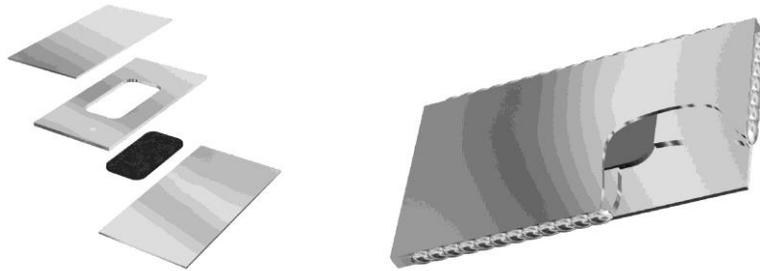


Figure 1 – Illustrating diagram of picture-frame technique to produce ^{99}Mo targets

The IPEN target is in its design phase. The preliminary neutronic calculations have already been made and revealed the amount of uranium that will be placed in the core of this dispersion. In general, the miniplates targets $\text{UAl}_x\text{-Al}$ are planned to have a total weight of 2.0 g of ^{235}U , or about 10 g total uranium metal (^{LEU}U -20wt% enriched with ^{235}U ; the remainder part is 80 wt% of ^{238}U). The uranium density is planned to be about 2.8-2.9 $\text{g}^{LEU}\text{U}/\text{cm}^3$. 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).

Another target reference, quoted also by Domingos, is the amount of metallic uranium is the target U-Ni thin sheet, which follows the post irradiation acid dissolution. These targets contain about 13 $\text{g}^{LEU}\text{U}/\text{unit}$. The thin foil target U-Ni evolved significantly over the past years, since it has been first developed by Cintichem firm, modified and patented in 90's by Argonne (4; 5). There are irradiation tests showing problems related to welding U-foil with Ni-foil (6). Conceptually, in Chilean project (7), this target is a thin foil of uranium of 60mm x 100 mm x 135 μm wrapped inside a 15 μm nickel foil, which is placed in a sealed aluminum tube for irradiation. The concept has been well developed in other countries. Presently, Chile (7), development effort are outstanding, but it is still in the testing phase. The Chilean system is shown Figure 2.

Target irradiation system

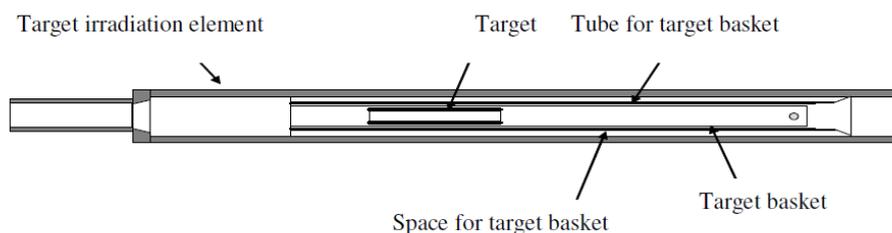
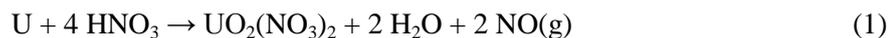


Figure 2 - Chilean System for irradiation system (7)

There is an inherent disadvantage of post-processing process using the target UAl_x -Al dispersion in relation to U foil-Ni, since the aluminum and its alloys use alkaline dissolution route, generating potentially losses of ^{99}Mo incorporated with solid waste, as well as it produces large quantities of high alkaline liquid radioactive as waste. In addition, the alkaline dissolution produces considerable hydrogen production, as a subproduct, which evolves during aluminum dissolution process in alkaline media. On the other hand, the acid route for post-processing U/Ni foil targets generates lower volumes of waste with better yields than the alkaline route. As a disadvantage, this route makes it necessary to treat nitrogen oxides in gaseous form (1). The route of acid dissolution dissolving nickel and uranium, follows the following reactions:



Based on these data, the present study aims to develop a uranium target with metallic powders, in the form of powder briquette of metallic uranium powder inside of a nickel powder compact. All this sets are covered by Ni-electrodeposition, sealing the assembling and avoiding the radioactive gas leaking from the assembly, facilitating so the handling during post-processing to produce the radionuclides pair ^{99}Mo - ^{99m}Tc . As the amount of Ni to be separated from uranium is relatively small, then, the post-processing of this target can be accomplished with relative ease and even can be separated during the dissolution with segmented time since nickel dissolves 8 times faster than uranium, as indicated Leonard et al. (8)

Nickel electrodeposition

During Ni-electrodeposition (9; 10; 11; 12; 13; 14) is known to form two crystal structures of nickel crystals (Nickel α and β). Nickel- α is a solid solution with low content of interstitial hydrogen. This α -phase obeys the kinetics of three-dimensional progressive nucleation and growth. Nickel- β is rich in interstitial hydrogen; its formation is favored by low pHs. It forms during initial electrodeposition process with high cathodic overpotential. It is interesting to have a higher proportion of nickel- α which is a more stable phase (dissolution in $-0.1V_{SCE}$) than the nickel- β before it dissolves at $-0.2V_{SCE}$. So, it dissolves earlier in a sweep towards anodic direction.

From the technological point of view, the DC electrodeposition is quite slow and, in terms, it is less reproducible to form a more continuous layer structure. After imposing an applied potential or a current to the electrode of interest, the concentration profile of the various electroactive species changes with time until it is stabilized by the balance of faradaic, diffusional and convective processes. On the other hand, the pulsed electrodeposition (15; 16) is a non-steady state electrochemical situation. The current or potential vary with time and the diffusion layer changes from moment to moment. The interest for non-steady state electrodeposition (17) is that it allows varying and controlling the structure and properties of deposited layer, including hardness, grain size and so on. Moreover this kind of process allows accelerating the film growth in comparison to DC current.

Application of cathodic currents i_c during t_c period and followed by an anodic (i_a , t_a) rectangular pulse, is considered as pulse current. It, in fact, includes the $i_a = 0$, which is an "off" situation. The deposit growth only happens if the charges balance is $q_c > q_a$ ($i_c t_c > i_a t_a$). So, the average cathodic direct current during the process gives the efficiency of the deposit, evaluated by:

$$i_{av} = \frac{(i_c t_c - |i_a| t_a)}{t_c + t_a} \quad (3)$$

Under pulsed regime, the current density in a cathodic pulse can be very high, 10 to 100 times more than the limiting current, but the corresponding pulse duration however is very small, less than the transition time, which is in the order of seconds. The graph for the concentration at the solution near the deposition surface varies. This is schematically in Figure 3.

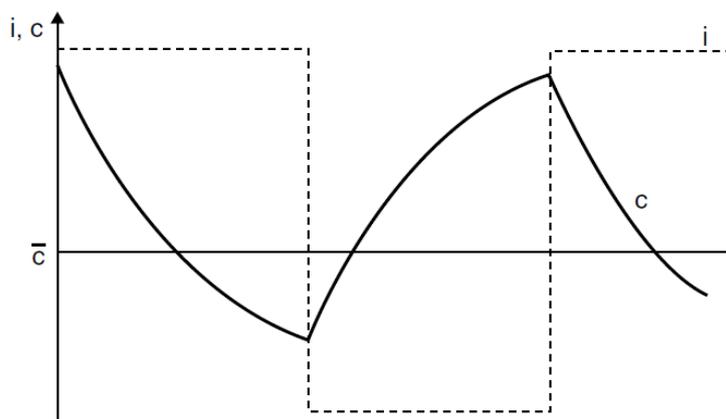


Figure 3 – Time variation of solute in deposition solution during rectangular on/off pulse. (17)

The average current density is always less than the limiting one, therefore it is impossible to accelerate the deposition rate by applying higher pulsed currents. The pulsed current can be effective, not to thicken the deposit thickness of metal films at the limiting current, but to create higher nucleation rate. This deposit results in a much more fine-grained one.

During the pause (or anodic pulse) following the cathodic pulse, the concentration in the diffusion layer restores its initial value by diffusion processes, since the material dissolved during anodic dissolution has no time to migrate far from the surface. During this moment, other processes may also be active at the electrode, for example, it may occur desorption of a surface-active. When a maximum adsorption corresponds to a certain maximum potential during the pulse, surface passivation may happen, since the dissolved oxygen adsorption that may occur. Additionally, side electrochemical processes can continue, because the saved electrical energy in the double layer, acting as capacitor discharging, promotes faradaic process. The use of anodic pulses is often very effective in achieving very smooth deposits with minimal structural defects. This is due to the dissolution, during anodic pulse, which are more active in defective areas or peaks on the surface. If that peaks were formed on the surface during a previous cathodic pulse, it would later grow into dendrites or sharper areas, but when followed by an anodic pulse, they allow dissolution of the peaks at first place because of their higher free energy.

In summary, three factors influence the structure and properties of the deposited layers using a pulsed current: the surface concentration of the electroactive ions, current microdistribution at the electrode surface and adsorption of surface active additives.

2. EXPERIMENTAL

Iron powder, with particle size of 37 μm , were compacted into briquettes by a press of 10 metric tons press having a die of 22mm in diameter. The briquettes were produced from lots of 4.1 g of material, giving compacts with 2.0mm in thickness, with a total area of 8.98 cm^2 . These briquettes were subjected to Ni electrodeposition pulsing process in an assembly shown in Figure 4. The solution for nickel depositing was the Watt's bath ($0.85 \text{ mol.L}^{-1} \text{ NiSO}_4 \cdot 6\text{H}_2\text{O} + 0.15 \text{ mol.L}^{-1} \text{ NiCl}_2 + 36 \text{ g.L}^{-1} \text{ H}_3\text{PO}_4$) with $\text{pH}=3.7$. The material was submitted to 10 repetitions of pulse electroplating at 900Hz, using a peak current of -0.84 A/cm^2 and duty cycle of 0.1, what resulted in a time "on" of 10^{-4} s and "off" of 10^{-3} s . It developed an average cathodic current of -0.744 mA/cm^2 during the experiment giving a typical graph against time as shown in Figure 4(b). The total experiment time was around 8 min for all 10 steps.

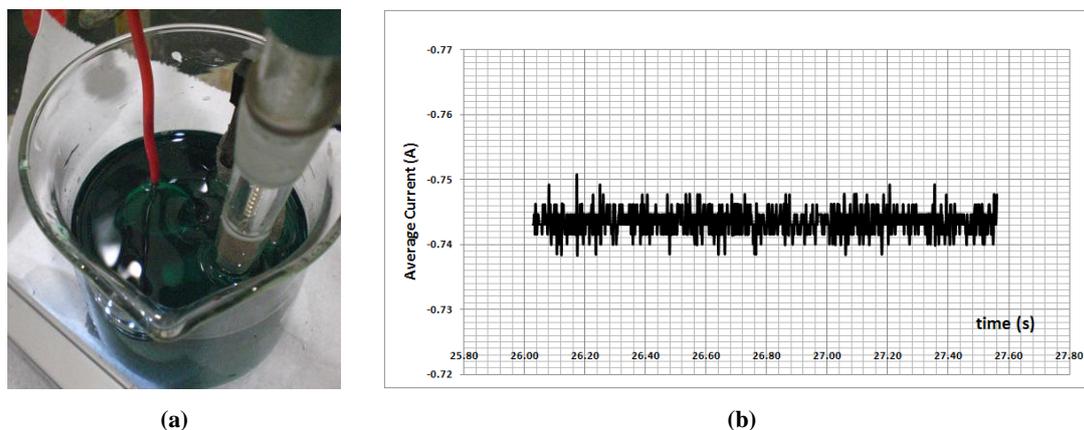


Figure 4 – (a) Electrochemical Cell assembled with the powder compacted briquette as the work electrode inside the Watt's bath as the solution for nickel depositing. (b) Average current registered during experiment.

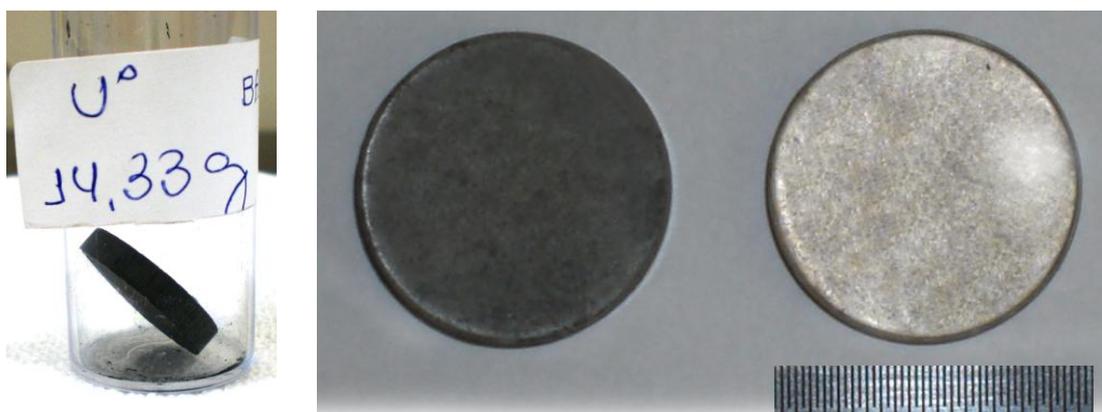


Figure 5 – (a) Uranium compact made from hydrated metallic uranium powder. (b) Iron-compact before and after the pulsing Ni-electrodepositing

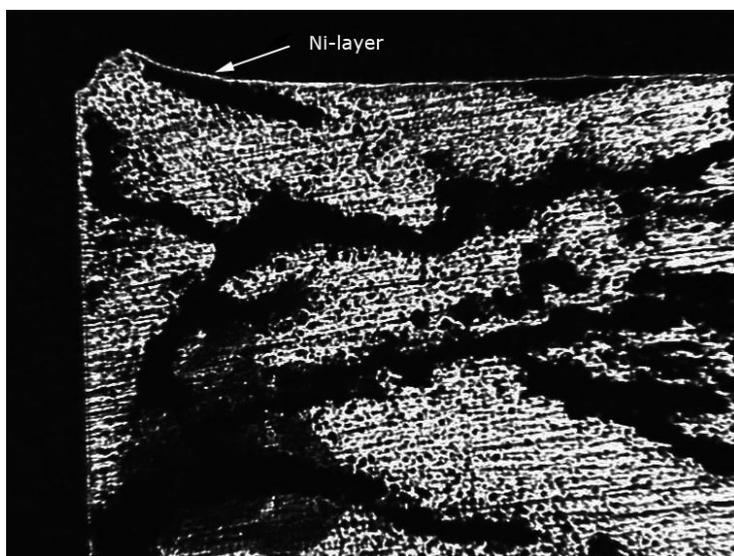
A uranium compact was also made with metallic uranium powder, obtained by hydrating, having 14.33 gU and it was also submitted to Ni-electrodeposition as made for Fe-briquettes. The Figure 5(a) shows the U-briquette and the Fe-briquette, before and after the deposition.

3. RESULTS AND DISCUSSION

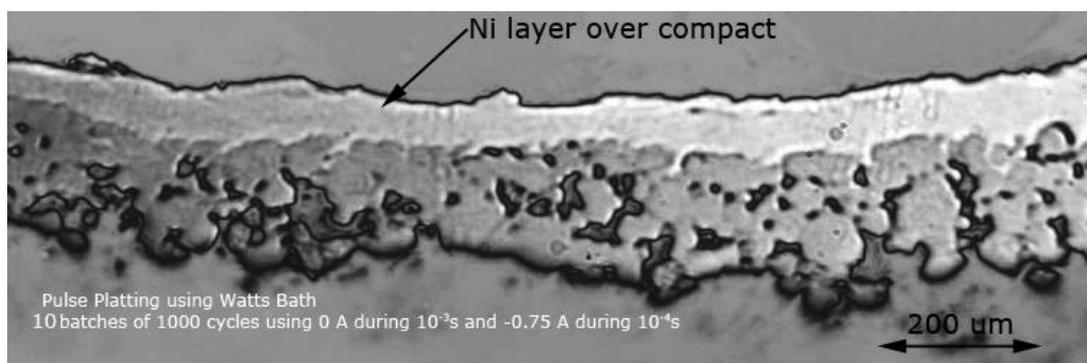
Typical samples of Fe-briquette with produced Ni-electrodeposits by “on/off” by pulsing technique are shown in Figure 6.

As it might be observed, the Ni-layer is around 100 μm in thickness. Figure 6 (a) shows, in a larger scale, the prepared metallographic sample. It gives a general idea how thin the layer is and how continuous it developed. During the cutting and polishing of the sample many parts of the compacted powder briquette was withdrawn from the surface and are, in the micrograph image, represented by the black regions. The Ni-layer continuity proved to be very resistant to the abrading and polishing materials during the preparation of the metallographic sample. It is

interesting that a process that lasted only 8 minutes produced a quite resistant barrier to the evolving fission gases, probably blocking the evolution of ^{140}Xe which is a neutronic by-product of ^{235}U fission. Other information from Figure 6 (b) is about the penetration of the layer towards the bulk of the compact, which is less than 400-500 μm , since the briquette material disaggregates easily beyond this limit.



(a)



(b)

Figure 6 – Microestrutura de pulsed Ni-electrodeposition over an iron briquette. (a) Ni-layer over a corner of the briquette with 30X magnitude. (b) the same Ni-layer in detail.

An important observation may be seen at Figure 6, where the layer shows itself very consistent in terms of microstructure. The pulse technique of nickel electrodepositing, as commented from the literature, formed a great number of nuclei sites, which promoted a very fine grain structure. This structure has its powder components size much less than 37 μm , which is the iron powder particle size, which was used to make the compacted briquette. Some of these iron particles could be seen in the micrograph, revealing indirectly the fine structure of Ni-layer pulse deposited.

On the other hand, doing the same pulsing sequence with the prepared uranium briquette, the results were unsatisfactory. The uranium briquette, as soon as it was immersed into the Watt's solution, it oxidized quickly as normally expected for uranium and uranium alloys. It so created an oxide layer over the compact and inside. All electrical contact was then lost since the oxide layer became quickly insulator. As a result, no Ni-electrodeposited layer was formed. The

uranium briquette disaggregated completely in less than 48 hours due to the remaining solution in its porous interior.

4. CONCLUSIONS

The pulse Ni-electrodeposition is a good process to coat powder material compacts. It produces a resistant and tenacious layer of 100 μm and it penetrates the briquette in less than 500 μm . It proved to be adequate to Fe-briquettes, but when this process was used to create a layer over the uranium-briquette the process was unsuccessful. As soon the uranium briquette was immersed in Watt's bath, immediately oxidized and impeded the electrochemical Ni electrodeposition. Other methods should be conceived, to create layers or protections in order to cover uranium compact before the electrodeposition of nickel should be made.

5. ACKNOWLEDGMENTS

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