USE OF ELECTRODEPOSITION OF NICKEL IN THE MANUFACTURE OF LEU ANNULAR TARGETS

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ABSTRACT

This work presents the results of a thin electroplated layer of nickel on the surface of the uranium to achieve deposits 15 to 25 μm thick. Ultrasound tests and electron microscopy showed good adhesion and homogeneity of the Ni deposit, which has high hardness and relatively small grain size, with an orientation in the direction of current flow.

Keywords: *Electroplating, uranium, nickel.*

INTRODUCTION

Besides its use as fuel in research nuclear reactors, uranium is used for the production of fission [99]Mo, which decays to the metastable isotope technetium-99m (Tc-99m), which is the most widely used radioisotope in nuclear medicine[1,2]. Medical diagnostic imaging techniques using technetium-99m account for roughly 80% of all nuclear medicine procedures, representing over 30 million examinations worldwide every year. Local production of this medical isotopes, which have half-lives of 66 hours for molybedenum-99 (99Mo) and 6 hours for its daughter isotope, technetium-99m (99mTc), and thus must be produced continually, could avoid cancellations or delays in important medical testing services[3].

Over the last five years the Chilean Commission Nuclear Energy (CCHEN) has been working on the development of the production technology of [99]Mo by irradiation of annular targets that contain low enriched uranium (LEU) foil. The main objective is to become a local producer of [99]Mo on a small scale, to satisfy the country's nuclear medicine and in that way reduce its dependence on foreign supplies. The annular target consists of two concentric tubes made of type Al-3003 structural aluminium which in a specially machined inner space contains a thin metallic LEU foil covered on both sides with a nickel foil that acts as a contention barrier for the fission products generated during irradiation.

In the irradiation tests it has been difficult to remove the uranium foil from the target, perhaps because of the joining of the uranium foil with the structural aluminium due to the mixing of ions caused by the escape of fission fragments from the uranium foil. For that reason nickel is used as a barrier against the escape of the fission fragments, located between the structural Al tubes and the uranium foil. The thickness of this barrier is determined by the recovery range of the desired fission fragments. The maximum recovery distance is approximately 7 μm, but to provide a safety margin a 15 μm foil thickness was established, which is twice the maximum layer. That layer must cover completely the uranium foil to avoid the possibility of localized joining with the structural Al. This compound material must have a uniform thickness to guarantee the proper fit with the purpose of facilitating assembly and having adequate heat dissipation during the irradiation[4,5]. The annular targets with nickel as barrier have good performance under irradiation from the heat transfer standpoint, in addition to avoiding the joining of the uranium foil with the structural aluminium during irradiation[6,7].

In the CCHEN the results so far indicate that the stages that require more careful attention from the technological standpoint correspond to assembling and welding the annular targets, mainly concerning the nickel foil used as a barrier against the escape of fission products. The reasons for this are the following: the most stringent specification in the assembly stage of the annular targets corresponds to the air space, which allows a very low tolerance, 0.006 – 0.020 mm, between the U-Ni set and the Al-3003. As a consequence of this there is a very narrow opening through which the U-Ni set can go. So during the assembly of the annular targets there is an operational problem that refers to introducing the U-Ni set without the Ni foil getting wrinkled or becoming cracked. For the welding stage of the annular targets the results show some porosity imperfections which according to the analyses made are caused by the release of impurities present in the Ni foil due to the temperature reached in the process. It is therefore presumed that this is the cause that does not allow an adequate welding bead in the annular targets.

In the CCHEN the development of the technology for making annular targets is focused on replacing the Ni foil by an electrolytic nickel layer that must be characterized so that it fulfils the specifications for being an effective barrier against the escape of the fission products. Consequently, the electrodeposition of Ni on uranium foil is aimed at solving the technical details described above and in that way improve production times and the quality of the annular targets.

EXPERIMENTAL PROCEDURE

To perform the electrodeposition a system composed of two cells that contain the electrolyte, one to heat the electrolyte and control the pH of the solution and the other to make the electrodeposition. The heating was done by means of a coil through which water heated by a copper heater was circulated.

Stirring took place by recirculation of the solution between the two stainless steel cells. The anode, which corresponds to the positive electrode in which oxidation takes place, was built with 2 stainless steel baskets that contain nickel tablets, because if an anode that does not dissolve during the electrodeposition process is used, the nickel salts are converted, due to the effect of the electrolysis, into the free acids, sulphuric and hydrochloric, allowing two phenomena to take place: decreased pH because acidity increases, and decreased salt concentration, affecting the efficiency of the process[8]. Uranium foil of approximately 100 x 50 x 0.12 mm was used as cathode. The electrodeposition system can be seen in greater detail in Figure 1.

The electrolyte was a solution with 250 g/L of nickel sulphate, 60 g/L of nickel chloride, and 40 g/L of boric acid in deionised water. The solution also contained 2 mL/L of Omega additive, which gives ductility and semi-gloss to the Ni deposit, and 4 mL/L of wetting agent to lower the surface tension of the Ni solution, thereby avoiding pore formation in the deposit. The nickel sulphate is the main source of Ni ions in this solution, while the nickel chloride contributes to dissolve the activated forms of nickel and the boric acid stabilizes the pH of the solution. The initial parameters used were those recommended for industrial electrodeposition[9], i.e., pH 4.0; temperature 40 °C, approximate voltage 2.0 V.
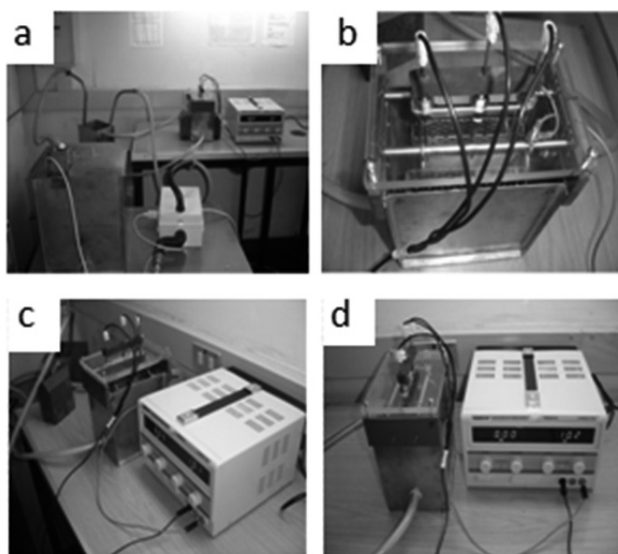
Figure 1.- Electrodeposition system.
a).- General overview, b).- Electrolytic cell, c).- Lateral overview of electrolityc cell and direct current power device, d).- Frontal overview of electrolytic cell and direct current electric power device.

The 100 x 50 x 0.12 mm uranium foil was subjected to surface cleaning with 65% HNO_3 during 10 minutes to remove the oxide layer, and the electrochemical experiments were performed immediately after. A Hewlett Packard power supply was used. Control of pH and temperature was made with an OAKTON pH/mV/°C meter. A PGP201 Radiometer Potentiostat/Galvanostat connected to a microcomputer with the Volta Master 1 software was used for the electrochemical test. All the measurement, unless otherwise mentioned, are referred to the saturated calomel electrode (SCE). Characterization of the deposits was performed by measuring the thickness with a Karl Deutsch Leptoskop 2041 model film thickness meter, a linear comparator, and the deposit was also characterized by a Meiji MT7000 metallographic microscopy, Jeol 5410 scanning electron microscopy, and ultrasound.

RESULTS AND DISCUSSION

In Figure 2a is possible to observe an area of reactivity that occurs in the first 1000 seconds after dipping the uranium in the solution of nickel. Finally the equilibrium potential obtained is in the range of -0.33 V_{SCE}.

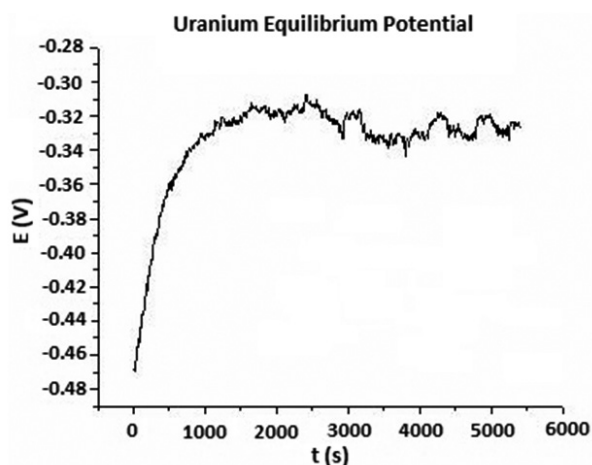**Figure 2a.-** Equilibrium potential of uranium, V_{SCE}.

Figure 2b shows the Eh-pH diagram of the system uranium in water. In this diagram it is possible to observe that the compound stable throughout the pH range is UO_2. This confirms the equilibrium potential values for uranium presented in Figure 2a. These results confirm the need, on the uranium foil the attack with HNO_3 solution to remove surface oxides.
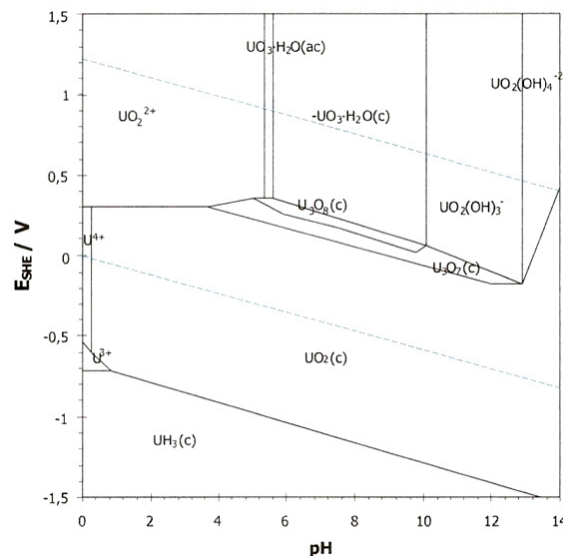

Figure 2b.- Eh-pH diagram for system uranium in water at 25 ºC.[10]

A cathodic polarization curve of the U-Ni system was obtained using a three-electrode system: uranium foil as working electrode, saturated calomel electrode (SCE) as reference electrode, and stainless steel baskets with nickel in them as counterelectrode, in other words, the same cell and electrode arrangement that will be used to perform the electrodeposition of nickel on uranium tests. The purpose of this polarization curve is to determine the limiting cathodic reduction current of Ni on uranium under the same operating conditions of the electrolysis in order to find the most adequate operating current to produce the best possible nickel deposit. This method was used in other system with good results[11].

Figure 2c shows that the limiting cathodic reduction current of Ni over U is approximately 90 mA/cm², so according to industrial operation criteria, the work should be done at a fraction of that limiting current, between ¼ and ¾ of that limiting current, i.e., between 22.5 and 67.5 mA/cm².

It was decided to work at current densities of 30, 32 and 34 mA/cm², because according to Winnand [12], with the purpose of ensuring good adhesion and low hardness of the Ni deposit, the lower end of the range, or ¼ to ¾ limiting cathodic current, should be used.
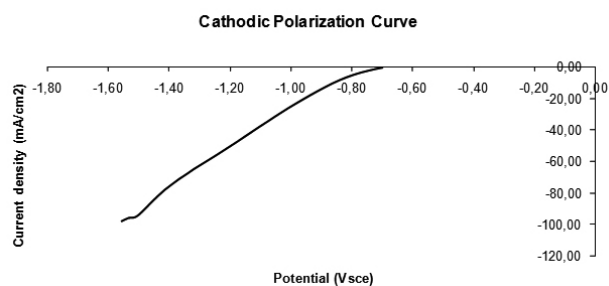

**Figure 2c.-** Cathodic polarization curve of the U-Ni system.

Table I presents the results of the experiments carried out on natural uranium foil according to the sequence shown in Figure 3. It is seen that the deposited mass approaches closely that foreseen by Faraday's law, but the thickness of the nickel deposit measured with the Leptoskop equipment differs

from that calculated with Faraday's current and time, and this is attributed to the fact that even though uranium has very low electric conductivity compared to Ni, the method of measurement considers the substrate and coating as no conducting and conducting. The Omega additive used actually improved substantially the appearance of the deposit, producing a cleaner and shinier surface, as shown in the last photograph (f) of Figure 3.

Table I. Results of the electrodeposition of Ni on U

| ID	I (A)	t (min)	M (g)	e* (μm)	M** (g)	e** (μm)
11.2	3.0	30	1.5	32.3	1.6	18.4
12.1	3.0	40	2.0	45.7	2.2	24.6
10.1	3.2	30	1.6	14.7	1.8	19.7
12.2	3.2	40	1.9	57.5	2.3	26.2
11.1	3.4	20	1.4	9.4	1.2	13.9
8	3.4	30	1.8	39.2	1.9	20.9
12.3	3.4	40	1.9	78.1	2.5	27.9

* Experimental measurements made with the Leptoskop; ** Faraday's law calculations.
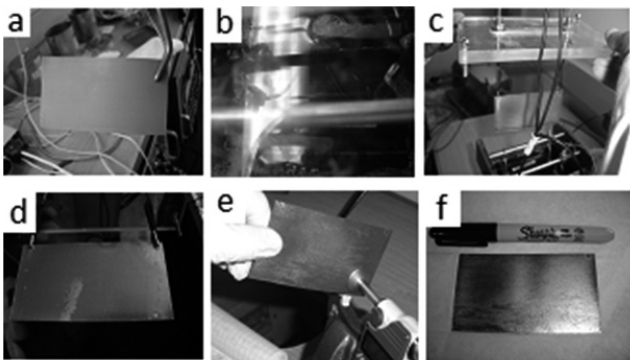
Figure 3. Sequence of the electrodeposition of Ni on U. (a).- Attacked uranium foil, (b).-Cell with nickel electrolyte, (c).- Uranium electrode device, (d).- Plated uranium with nickel, (e).- Measuring of deposit with the Leptoskop equipment, (f).- Final plated uranium with nickel.

The superficial distribution of the thickness of the nickel coating for foil 11.2 is shown in Figure 4. The average value was 32.3 μm, from a sample population of 24 points for the 50 cm² area.

Most of the values fit around the center of the 30-40 μm range. The superficial distribution of the Ni deposit is quite homogeneous and the largest values are found in the bottom part of the foil, showing that the ion flow has an expected trajectory[13].
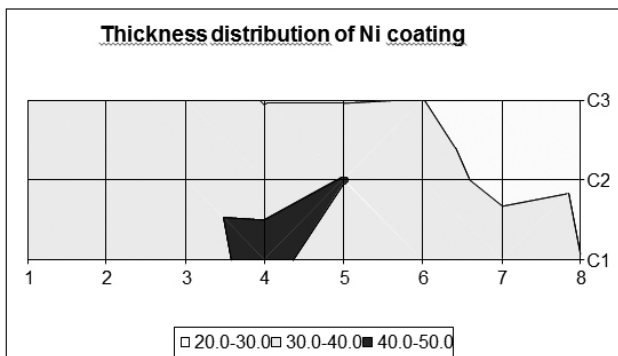

Figure 4. Surface distribution of Ni coating on uranium

Ultrasound studies were made to determine the degree of adherence of the Ni deposits on uranium. Figure 5 is an image of a linear C-scan of sample 12.2 which shows a signal without discontinuity, which indicates qualitatively that there is good adherence of the deposit.

The micrograph of Figure 6 corresponds to a cross section of sample 8 which shows the surface of the uranium with a Ni deposit on both sides, which appear quite homogeneous in thickness that ensures adequate fit and adequate heat dissipation as shown J.A. Smaga et al. [4].
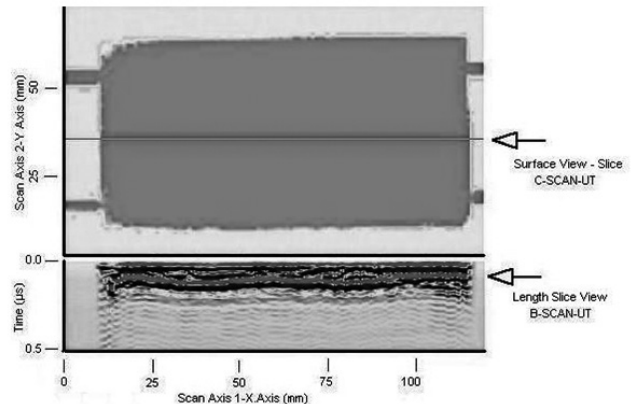
Figure 5.- C-scan image of sample 12.2.
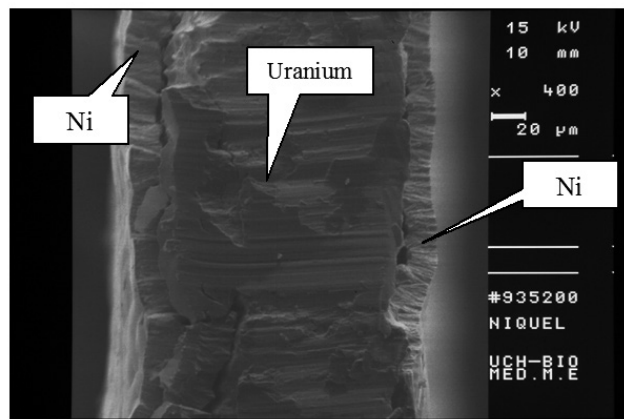
Figure 6.- Micrograph of cross section of sample 8

The orientation of the deposit follows the trajectory of the current flow, and therefore the grain size of the deposit is relatively small [9].

The surface of the deposit is free of pores and is in layers that form valleys and hills, as seen in the micrograph of Figure 7, in agreement with what was found in the ultrasound C-scan signal of Figure 8. The addition of the wetting agent confirms what was indicated by Kanani[13] on the influence of a surfactant on the surface tension between the substrate and the electrolyte, in this way minimizing the existence of defects caused by the presence of hydrogen.

The Vickers microhardness of the Ni deposit as a function of current intensity was determined applying a 500-gram load. Table II shows a direct relation between the current intensity applied in the electrodeposition process and the hardness of the Ni deposit, indicating that the higher the current intensity, the smaller the grain size of the deposit, and consequently the hardness increases.
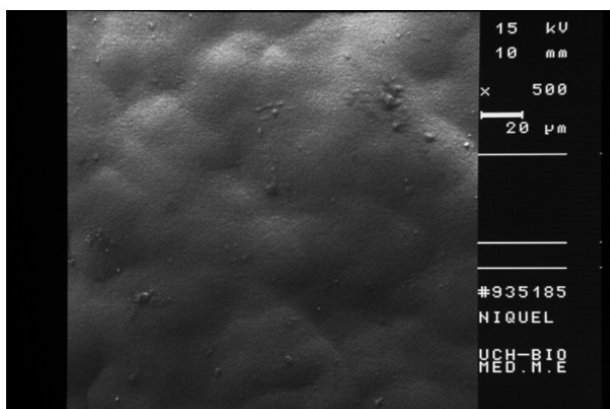
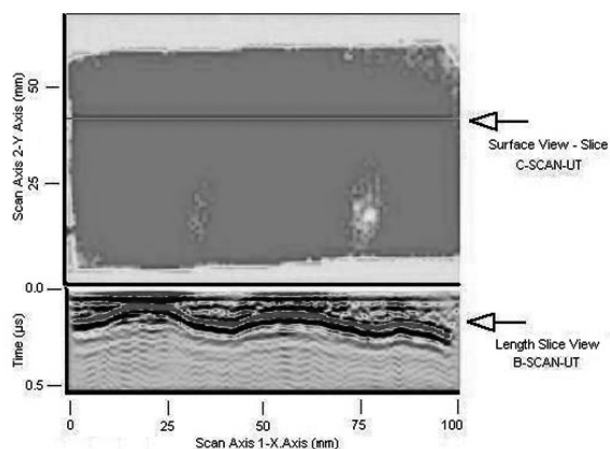**Figure 7.-** Surface micrograph of sample 11.1.

Figure 8.- C-scan image of sample 11.1.

Table II. Hardness of Ni deposit as a function of the applied current intensity

ID	Hardness (HV-0.5)	Current (A)
12.1	398.3	3.0
12.2	406.7	3.2
12.3	426.7	3.4

CONCLUSION

The electrolytic coating of thin uranium foil with nickel is feasible, yielding a homogeneous Ni deposit with good adherence and free of porosity.

ACKNOWLEDGEMENTS

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