PREPARATION OF URANIUM COATINGS BY ELECTRO DEPOSITION IN MOLTEN CHLORIDE MEDIA

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Introduction:

The electrodeposition of uranium is now a relevant topic for two kinds of applications: (i) the preparation of this metal with compounds extracted from the mineral ores; (ii) the separation from lanthanides in the nuclear waste.

This paper concerns the process of preparation of uranium metal on various substrates, using the electro deposition process in molten salts. The electrolyte consists of an eutectic mixture NaCl-KCl as solvent (fusion point 650°C) and a tetravalent uranium compound, UCl₄, as solute. We present the results, theoretical and practical, necessary to manage the process. So, the following points will be considered stepwise in this paper:

- The electrochemical behaviour of uranium III ions in the electrolyte, since it is now clearly established that uranium metal can be prepared by electrochemical reduction of UCl₄ in a NaCl-KCl mixture in a single step process: \( U^{III} + 3 \text{e}^{} \rightarrow U^{0} \) \[1,2\] .

- The crystallisation mode of uranium on the cathodic material.

- The preparation of uranium coatings with variables conditions: temperature, electrolyte concentration, current density and cathodic substrate.

- The observation of the crystal growth on the substrates, by using SEM micrographies.

More detailed developments of these results should be found in references [3-5]
Experimental details:

- The electrolytic bath: it was composed of a eutectic mixture of NaCl and KCl (50/50 mol/mol) as solvent and UCl₄ as solute.

Granules of uranium metal, always kept in excess, were placed in the crucible in order to produce trivalent uranium according to the following reaction:

\[ 3\text{UCl}_4 + \text{U} \rightarrow \text{UCl}_3 \]

Uranium tetrachloride was introduced through an air-lock into the melt under argon.

The bath was initially dehydrated by heating the mixture of salts up to its melting point (658 °C) under vacuum (4.10⁻² mbar).

- The cell: the electrolyte was contained in a vitreous carbon crucible placed in a graphite chamber inside a cylindrical refractory steel chamber; this arrangement prevents the attack of the inside wall of the chamber by molten salts vapours. The cell was closed with a water-cooled stainless steel lid.

The experiments were performed in an inert atmosphere of grade U argon previously dehydrated and deoxygenated using a purification cartridge (Air Liquide).

- Electrodes: For analytical purposes: the working electrode was 1 mm diameter wire of tungsten or 3 mm diameter vitreous carbon rod (dipped 1 cm into the bath); the comparison electrodes was a platinum wire, with a potential fixed by the Pt(II)/Pt system [6]. The auxiliary electrode was a vitreous carbon rod with a large surface area (2 cm²). For electro deposition runs, we have used: as cathodic materials, 2 cm² sheets of steel, stainless steel and copper or vitreous carbon rods (2 cm²), as anode, the vitreous carbon crucible.

- Electrochemical methods: We used successively, for the investigations on the electro reduction process cyclic voltammetry, chronopotentiometry, and square wave voltammetry, for elucidating the nucleation process, chronoamperometric measurements and intensiostatic electrolysis for the electrodeposition of uranium thick coatings.

- Structural Analysis: Uranium deposits were observed by Scanning Electron Microscopy (LEO S440); the cross section of the layers were examined by Energy Dispersive Spectroscopy (Oxford Link System) and by X-ray diffraction (Siemens D 500).

Electrochemical reduction process of U⁰ ions in molten chlorides.

The electrochemical behaviour of uranium III ions in molten chloride baths can be described by the cyclic voltammogram of fig.1 which exhibits one pre peak, then one peak in the reduction sense (respectively Ic, IIc) associated to the oxidation peaks Ila and Ila, successively observed in the reoxidation sense of scanning potential.

According to the respective differences of potentials between the peaks Ia and Ic on one hand, IIa and IIc on other hand, we can conclude that the system I is irreversible.
while the system II is quite reversible. In order to elucidate the electro deposition process of uranium ions, we have identified each of these systems in ref [3]. We summarise here only the results of this investigation.

System I: the prepeak Ic is attributed to an electrochemical reduction of $U^{4+}$ in an adsorbed species of uranium; the growth of the adsorbed layer follows the Langmuir model, since the increase of the prepeak is limited when the content in uranium ions increases. Notice that the phenomenon is influenced by the cathodic material: for instance the position of the pre peak I is more anodic than peak II on silver, copper, molybdenum or vitreous carbon, similarly to that observed on fig.1, whereas it is more cathodic in the case of platinum (post peak). The adsorption of the electrodeposited species at more anodic potential than the metal is currently observed (underpotential electro deposition) and according to ref. [7], it is suspected to influence the future adherence of the electrodeposited layer.

System II: This system is associated to the formation of uranium metal onto the cathode, by the way of the electro reduction of trivalent uranium ion in the crystallized metal. Different techniques were used to characterize this reaction:

- **Cyclic voltammetry:** The linearity of the current peak with the square root of the scan rate of potentials (see fig 2), means that the electrode process is controlled by the diffusion of the electrolyte at the cathode interface and that the following equation (Randles-Sevcik) is valid:

$$i_p = \frac{0.61(nF)^{3/2}(RT)^{1/2}AD^{1/2}C_0}{\sqrt{v}}$$

where $n$ is the number of electrons involved in the reaction, $F$ is the Faraday constant, $R$ is the gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$), $T$ is the temperature in Kelvin, $A$ is the electrode area ($\text{cm}^2$), $C_0$ is the bulk concentration of the electroactive species ($\text{mol.cm}^{-3}$).

- **Chronopotentiometry:** On fig. 3, we observe the potential response to a high cathodic current pulse, followed by the same reverse anodic pulse; The durations of the potential plateaux ($\tau_{c}$ and $\tau_{a}$), corresponding to the respective cathodic and anodic reactions, are equivalent, meaning that the reaction is associated to a phase change, likely the formation of a metal. The potential variation on the cathodic plateau obeys the Sand equation:

$$iV = 0.5\pi^{1/2}nFC_0D^{1/2}$$

Combining equations (1) and (2) gives

$$i_p / \sqrt{v} = K\sqrt{\tau}$$

with $K = 41.95 \sqrt{T}$ and allows the number of electrons to be calculated. We find that 3 electrons are exchanged in the temperature range 680°C - 716°C. Then, using each equation, we can calculate the diffusion coefficient of trivalent uranium in the electrolyte. Table (I) gives an average value of $D$ at 715°C, obtained by each method, in good agreement.
Table (1): Measurements of diffusion coefficient of uranium III at 715 °C.

- **Square Wave voltammetry** has confirmed these results [1]

### Electrochemical nucleation of uranium in molten chlorides.

Once the electro reduction process achieved, the step of formation of nuclei (nucleation step) takes place, giving rise further to the crystallised deposit. The nucleation step can be observed by an electrochemical method, the chronoamperometry, which consists in measuring the current during a short potential pulse. Fig. 4 shows the transient currents on a vitreous carbon cathode, for various potential pulses. The shape of these curves is typical of successive nucleation and growth of a metal covering a foreign substrate. The overall curves include three parts:

- The initial regime of each transient is characterised by a sharp decrease in current which corresponds, after charging of the double-layer, to the formation of the first germs on the electrode (part I).
- This is followed by a rise of the current due to an increase in the electroactive area due to the growth of crystals on the electrode (part II). This rise in current culminates in a broad maximum, \( I_m \), the position of which on the time axis, \( t_m \), depends upon the magnitude of the potential step.
- Finally, in part III, the slow decrease of the current corresponds to the limitation of the reaction process by the semi-infinite linear diffusion of the \( \text{U}^{II} \) ions. The current time characteristic follows a linear relationship between \( I \) and \( \sqrt{t} \), typical of a diffusion phenomenon on the electrode surface.

It is possible to obtain a model of the nucleation step, correlating the two following adimensional ratios \( \left( \frac{I}{I_m} \right) \) and \( \left( \frac{t}{t_m} \right) \), \( I_m \) and \( t_m \), being the coordinates of the maximum observed on chronoamperograms; the following equations being valid in the respective cases of instantaneous and progressive nucleation [8]:

- **Instantaneous nucleation:**

  \[
  \left( \frac{I}{I_m} \right)^2 = 1.9542 \left( \frac{t}{t_m} \right) \left( 1 - \exp \left( -1.2564 \left( \frac{t}{t_m} \right) \right) \right) \]

  \[
  \frac{t_m}{t} = 1.2564 \left( \frac{N}{\pi \kappa D} \right) \]

  \[
  I_m = -0.6382 \pi F D C_0 (kN)^{1/2}
  \]

  with \( \kappa \) being the rate of incorporation of the metal ion in the lattice of the substrate (constant at constant potential) and \( N \) the density of nuclei.
Progressive nucleation:

\[
\left( \frac{I}{I_m} \right)^2 = \frac{1.2254}{t / t_m} \left[ 1 - \exp \left( -2.3367 \left( \frac{t}{t_m} \right)^2 \right) \right]^2 \tag{6}
\]

\[
t_m = \left( \frac{4.6733}{\Lambda N_0 \pi k'D} \right)^{1/2} \tag{7}
\]

\[
I_m = -0.4615 \frac{nFD^{3/4}C_0(k'AN_0)^{1/4}}{\rho} \tag{8}
\]

\(N_0\) being here the density of the favorable sites.

Experimental plotting, compared in fig. 5 to the theoretical curves, calculated with equations (3) and (6) (above) allows to conclude that the nucleation is instantaneous on a cathode of vitreous carbon.

Then it is possible to calculate the density of nuclei as a function of the over potential of the cathode, using the following equation, valid in the case of instantaneous nucleation in the part II of the chronoamperogram [9]:

\[
i = \frac{nF(2C_0D)^{3/2}\sqrt{M}}{\rho^{1/2}} N \cdot t^{1/2} \tag{9}
\]

Where \(M\) and \(\rho\) are respectively the molar weight and the specific weight of uranium.

Tables (2) and (3) give the density of nuclei on vitreous carbon respectively as a function of the overvoltage and as a function of temperature:

<table>
<thead>
<tr>
<th>(-\eta/\text{mV})</th>
<th>250</th>
<th>320</th>
<th>380</th>
<th>450</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^{-6}N/\text{sites.cm}^{-2})</td>
<td>3.6</td>
<td>6.8</td>
<td>7.4</td>
<td>8.7</td>
</tr>
</tbody>
</table>

Table (2): Influence of the over voltage on the density of the created nuclei; 
\(C_0 = 3 \times 10^{-5} \text{ mole cm}^{-3}; T = 670^\circ\text{C};\) cathode: vitreous carbon.

<table>
<thead>
<tr>
<th>(T/\text{°C})</th>
<th>670</th>
<th>685</th>
<th>700</th>
<th>715</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^{-6}N/\text{sites.cm}^{-2})</td>
<td>1.4</td>
<td>1.5</td>
<td>2.0</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Table (3): Influence of the temperature on the density of created nuclei; 
\(C_0 = 3 \times 10^{-5} \text{ mole cm}^{-3}; \eta = -170 \text{ mV};\) cathode: vitreous carbon.

We can note on these tables the strong influence of the parameters current density and temperature on the initial coverage of the substrate.

Figure 6 shows The SEM observation of the cathode after a short potential pulse: the nuclei formed at this short electrolysis time are probably on this micrography circular spots, white or dark, (dark when the nuclei were removed during the washing of the cathode). We can conclude that the repartition of the uranium crystals is quite uniform at the beginning of the electro deposition step.
Preparation of uranium coatings:

We report here some results and observations of our investigations on the electro deposition of uranium in NaCl-KCl-UCl₃ mixtures in the 670-710°C temperature range:

• The uranium deposits are not adherent, dendritic and their shape is anyway similar to fig. 7, larger at the bottom than at the top. The compactness, measured by the ratio \( \frac{\text{uranium mass}}{\text{overall deposited mass}} \) is not good (less than 50%) because a large quantity of salt is kept in the porosities of the coating.

• The current density of the electro deposition was between 50 and 400 mA.cm\(^{-2}\). We did not notice any influence of this parameter on the compactness of the coating; nevertheless, the current efficiency, measured by the ratio \( \frac{\text{experimental uranium mass}}{\text{theoretical uranium mass}} \) is always close to one.

• The adherence is slightly dependent on the cathodic substrate and should be correlated to the formation of an adsorbed layer (see above) or a surface alloy layer uranium, as in the case of copper (UCu₅), or stainless steel (U₆Fe). In these cases, we observe a quite adherent underlayer below the dendrites.

• The temperature influences somewhat the morphology of the dendrites: when the temperature is lower (670°C) the dendrites have the shape of fig 8-a (dendrite type 1); dendrites of type 2 are observed at higher temperatures (700-710°C) (fig. 8-b); at the intermediate temperatures, both types of dendrites are observed. This change was attributed to the transition temperature (668°C) where the change of phase \( \alpha \) in phase \( \beta \) occurs.

• The growth of the uranium coatings was observed at different times of electrolysis (fig. 9 and 10):

  (i) Short time; charge = 20 C (fig. 9):

  A thin layer of uranium is observed on the cathode (fig. 9.a.), we note that some parts of the substrate are not covered (dark zones). Magnification of fig.9.a shows that this layer is composed of nodules (fig. 9.b).

  (ii) longer time; charge = 200 C (fig.10) :

  Here the substrate is entirely covered with a layer of uranium and some faceted prominences appear which could be the base of dendrites (fig. 10.a).

On the magnification of fig. 10.a we see that it is composed of an agglomerate of grains of homogeneous size (fig.10.b). These grains arise from the growth of the nodules observed in the micrograph in fig. 6. The comparison of these two micrographs reveals that the increase in size of these nodules is anomalously low.
However, this can be explained by the fact that most of the current is used for the growth of the dendrites.

Conclusion

This work has showed that the preparation of metallic uranium by the electrochemical way is feasible from mixtures of chlorides containing trivalent uranium ions. The results obtained in the nucleation study prove that the nucleation of the electrodeposited metal is instantaneous, as frequently in electro deposition of most of metals. The good current efficiencies are attractive if we expect to use the electrolytic route both to prepare uranium or to separate this metal with lanthanides. We have now to correct the lack of compactness and adherence of the uranium deposits. These disturbances arise from the phenomena occurring during the growth of the layer, associated to the diffusion of the electrolyte next to the crystal growing onto the cathode; these phenomena were identified and modeled in recent works of electro deposition carried out in aqueous media [10]: the depletion of the electrolyte in the diffusion layer promotes both increase of the anion content and the decrease the cation content; strong local electric fields are generated, producing special motion of the electrolyte by electro convection and electro migration. The ramifications of dendrites and the fractal structure of the coating arise from the heterogeneity of the diffusion layer.
Fig. 1. Cyclic voltammogram of NaCl-KCl-UCI3 (2% mass), \( \theta = 700^\circ C \), \( S = 0.492 \text{ cm}^2 \), \( v = 200 \text{ mV/s} \), working electrode: W, reference electrode: Pt; counter electrode: vitreous carbon.

Fig. 2. Current of peak \( \text{I}_{\text{IC}} \) versus the square root of the scan rate \( v \), \( \theta =715^\circ C \), \([\text{U}] =1.5 \% \) mass, working electrode: W (0.5 cm\(^2\)), ref. electrode: Pt.

Fig. 3. Reversal chronopotentiogram of \( \text{UCI}_3 \) in NaCl-KCl, \( I = 169 \text{ mAcm}^{-2} \), \( \theta =715^\circ C \), \([\text{U}] =1.5 \% \) mass, working electrode: W, reference electrode: Pt.

Fig. 4. Potentiostatic current-time transients of NaCl-KCl-UCI3 at various cathodic overpotentials with 0.4 % mass of uranium on a vitreous carbon cathode at 670°C.

Fig. 5. Comparison of the dimensionless experimental data derived from the current-time transients with the theoretical models for instantaneous (1) and progressive nucleation (2) at different temperatures: \( \times 670^\circ C \); \( \circ 685^\circ C \); \( 700^\circ C \); \( \varnothing 715^\circ C \).

Fig. 6. Scanning electron micrograph (\( \times 680 \)) of uranium deposit on vitreous carbon at 670°C; \( \eta = 320 \text{ mV} \).
Fig. 7. Photograph of uranium deposit obtained on a steel cathode (Q=600°C, [U]=5% mass, \( \theta = 710^\circ \text{C} \), \( I=100 \text{ mA/cm}^2 \))

Fig. 8.a. S.E.M. of type 1 uranium dendrites

Fig. 8.b. S.E.M. of type 2 uranium dendrites
Fig. 9. S.E.M. of uranium deposit obtained by a short electrolysis: 44 s (charge: 20C). Electrolysis conditions: substrate, steel, TEMP= 690°C, C.D. = 225 mA cm$^{-2}$.

Fig. 10. S.E.M. of uranium deposit obtained by electrolysis: 7 minutes (charge: 200C). Electrolysis conditions: substrate, steel, TEMP= 690°C, C.D. = 225 mA cm$^{-2}$.
References