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Preparation of uranium targets by electro-deposition method

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Abstract In this paper, uranium targets are prepared by electro-deposition. Hydrated uranium dioxide films are electrodeposited into stainless steel plates using uranyl nitrate in ammonium oxalate solution. The results show that the deposition efficiency of the uranium depends on many parameters, such as pH value, supporting electrolyte, current density, and cell design. The uranium films were characterized by infrared spectrum, scanning electron microscope, and X-ray spectrum. The uranium films, with a yield of 98%, are in the thickness of about 6 mg·cm^{-2}.

Key words Electro-deposition, Uranium, target

1 Introduction

Most uranium targets are of enrich ^{235}U of over 90% [1–3], in a form of plate, and U-Al or UMg alloys with an aluminium shell. Making such a target by machining would be a complex process with considerable waste the valuable material. So, electro-deposition technique is widely adopted to make the targets [4–6], duo to advantages of using the fissile isotope in reactor fuel level, high deposition efficiency, smooth plating layers, and easily control[7–11]. Although it has been reported that ^{235}U targets in thickness of less than 1mg/cm^2 were prepared by electro-deposition[12], it is hard to prepare thick films by the electro-deposition. In this work, thick ^{235}U films were electro-deposited on stainless steel plates. The deposition temperature and time, and concentration and pH value of the electrolyte, were studied for optimizing the parameters.

2 Materials and methods

2.1 Materials

U_3O_8 was provided by Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics. Other chemicals, including ammonium oxalate, azoarsenic(III), nitric acid, acetone were commercially obtained and used without further purification.

UV-vis spectrophotometer (756 MC, Chelleson Scientific Instruments Co. China), temperature-controlling circular water shower (Shanghai Circulating Water Pump Factory, China), DSX-25 constant-velocity digital stirrer, power supply of the electrophoresis apparatus (DYY-8B, Beijing Glass Instrument Technology, Inc., China), scanning electronic microscope (SEM JSM-6490LV, Japan Electronics Co., Ltd., Japan), X-ray energy digital spectrum(EDS, GENESIS 2000 XMS, USA), Fourier infrared spectro-photometer (FT-IR, NEXUS470, Nicolet Corp. USA) were used for the analyses.

2.2 Experimental methods

Ammonium oxalate of 0.15 mol/L was used as the supporting electrolyte, added with 50 g/L uranyl nitrate (nuclear grade). As shown in Fig.1, the electro-deposition apparatus consists of a PVC base attached to a glass body, with a platinum wire (Φ1 mm) as the anode, and a polished Φ20 mm stainless steel disc as the cathode, which is held at the bottom with an O ring and a clamp. The straight Lucite tube has an outside thread to fasten a retaining metallic cap that holds the cathode plate. On the SS cathode plate, the only metal in contact with the electrolyte (~220 mL), an area of Φ15 mm can be deposited with ^{235}U.

One minute before switching off the current, 1 mL of concentrated NH_4OH solution was added to fix

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the deposited film and neutralize the solution. The cathode disc was removed, washed with distilled water and acetone, and dried under an infrared lamp at 200°C.

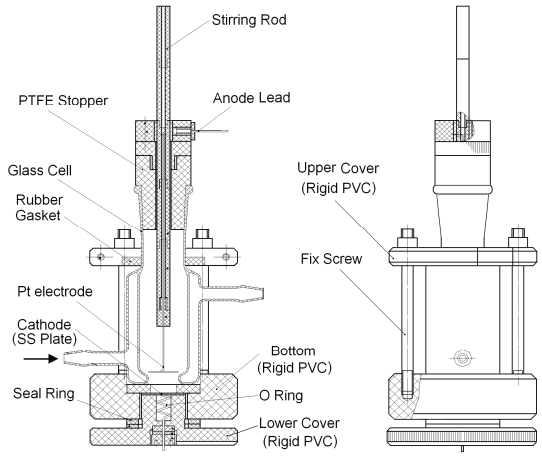

Fig.1 A schematic view of the electro-deposition apparatus.

2.3 Measurement and analysis

The electro-deposition yield of thick film samples was obtained by comparing UV-spectra of the electrolytic solution, and comparing weight of the SS disc, before and after the deposition.

The azoarsenic (III) plays an important role in the measurement. It forms a compound with uranium (VI) in HCl solution at pH 2–3, and the compound has UV absorption peaks at 660 nm. The peak heights are linearly correlated with the U concentration of $2.1 \times 10^{-8} – 4.6 \times 10^{-7}$ mol/L.

The uranium layer was examined by SEM. Uniformity of the layer was estimated using γ-ray spectrometry. Fastness of the deposition layer was checked by vibration tests.

2.4 Pretreating of the cathode

The deposition efficiency is affected by status of the cathode surface. A highly polished surface improves quality of the uranium films, while a scratched surface does the opposite, presumably because it favors the water splitting pathway by providing nucleation sites for gas evolution, and a deposited film has uneven appearance with speckles and may be unstable. To avoide oxidation of the cathode, it should be used for film deposition shortly after its pre-treatment of the following steps: (1) annealing at 500°C to reduce the inner stress of the stainless steel disc; (2) burnishing with sand paper; (3) wiping the surface with ethanol and acetone; and (4) plating nickel on the SS disc in the solution of 240 g/L 25 g $NiCl_2 \cdot 6H_2O$ and 60–80 mL/L HCl for 3 min at room temperature, keeping current density at 20 mA/cm^2.

3 Results and discussion

3.1 Effects of the deposition parameters

3.1.1 pH value of the electrolyte

Uranium films were deposited in electrolyte of pH 1–7 under the following conditions: current density (50 mA/cm^2); deposition time (3 h); and temperature (60°C). The result showed that the solution could have yellow floccules at pH values of > 4 or < 2, and adherence of the uranium films was poor. At pH = 2–3, the uranium films were uniform, adhering to the substrate nicely, with high depositing efficiency(~95%), the SEM images shows in Fig.2. The uranium ions and OH^- form hydroxide on the cathode in the electro-deposition process, but a high pH solution (pH > 4) prevents the hydroxide formation, while in a low pH solution (pH < 2) the hydrolysis products can diffuse farther from the cathode.

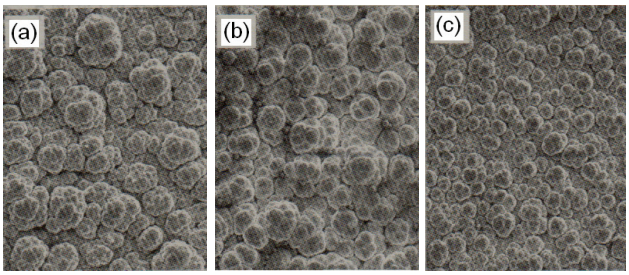

Fig.2 Effect of pH on the uranium target morphology, (a) pH ≈ 1.0, (b) pH = 5.0–6.0, (c) pH = 2.0–3.0.

3.1.2 Current density of electro-deposition

The uranium films were deposited under current densities of 40, 60, 80, 100 and 150 mA/cm^2, under the following conditions: deposition time, 6 h; pH=2–3; and temperature, 60°C. The results in Table.1 show that the film thickness increased with current density, but the film adherence to the substrate becomes worse at 40 and 150 mA/cm^2.

3.1.3 Temperature of the electrolyte

The films were deposited under pH = 2–3 and 60 mA·cm^2 at 40°C, 60°C and 80°C. Faster electro-deposition was observed at 60 and 80°C (Fig.3). The depositing efficiency reached ~98% in 2 h at 80°C, whereas the same result was obtained in 9 h at 40°C. The SEM images of the films deposited at different temperatures are shown in Fig. 4. The films

Table.1 Relationship between current density and quality of the plating layers.

Current density /mA·cm^{-2}	Film thickness / mg·cm^{-2}	Film appearance	Gravitational fall test from 1 m
40	4.589	Smooth surface, partial rough	A few falling off
60	4.796	Smooth, compact, firm, grayish-black surface	No
80	5.743	Smooth, compact, firm, black surface	No
100	5.948	Smooth, compact, firm, black surface	No falling off
150	6.682	Compact, firm, gray brown	Partial falling off

deposited at 40°C and 80°C were with a rough and incompact surface of many crackles, which would cause easy falling-off of the films. At 60°C, the film surface was smooth, with uniformly distributed crystal particles.

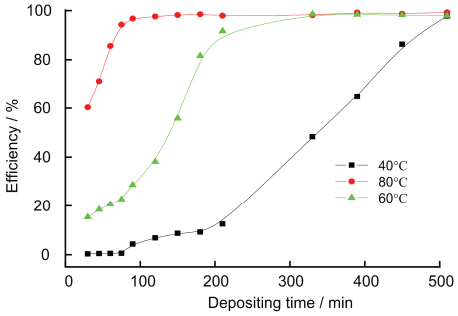

Fig.3 Effect of temperature and time on the uranium target deposition efficiency.

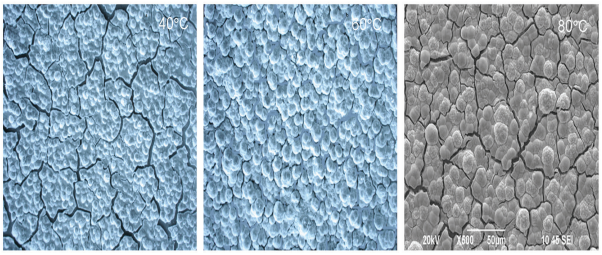

Fig.4 SEM images of uranium films deposited at different temperatures.

3.1.4 Concentration of the electrolyte

The $UO_2(NO_3)_2$ concentration in the electrolyte affected the uranium film deposition in a complex way, as shown in Fig. 5. The efficiency increased with the electrolyte molarity at lower concentrations, reached the maximum at 1.67 mg/mL, where it began to decrease with increasing concentration. In the low electrolyte concentration region, hence high resistivity of the medium, the electrolysis rate is high at relatively higher electrolyte concentrations with improved conductivity, whereas in the high electrolyte concentration region (>2 mg/mL), the solution had yellow floccules, which impacts the depositing efficiency negatively.

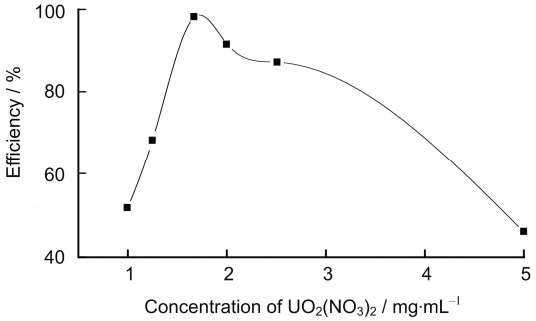

Fig.5 The effect of the concentration of $UO_2(NO_3)_2$ on electro-deposition of uranium.

Fig.6 shows the uranium targets of a deposition density of about 6 mg/cm^2.

Fig.6 The uranium targets.

3.2 Characterization of the uranium films

3.2.1 FT-IR

A typical FT-IR spectrum of a uranium film samples are given in Fig. 7, together with that of a uranium powder sample. The absorption peaks are: 3418 cm^{-1} (OH), (3169 cm^{-1} (OH, NH_4), 1619 and 1514 cm^{-1} (HOH), 898 cm^{-1} (UO_2), 487 cm^{-1} (UOH), 383 cm^{-1} (UO), and 267 cm^{-1} (UOH,UO_2). Its possible composition is $[UO_2(H_2O)_4\text{-}O\text{-}UO_2(H_2O)_4\text{-}O]$. From the FT-IR spectrum, the uranyl ions deposited on the cathode in hydrated polymer form, which is connected by oxygenic bridge. The oxidation state of the uranium is based on the binding energies for both U and O.

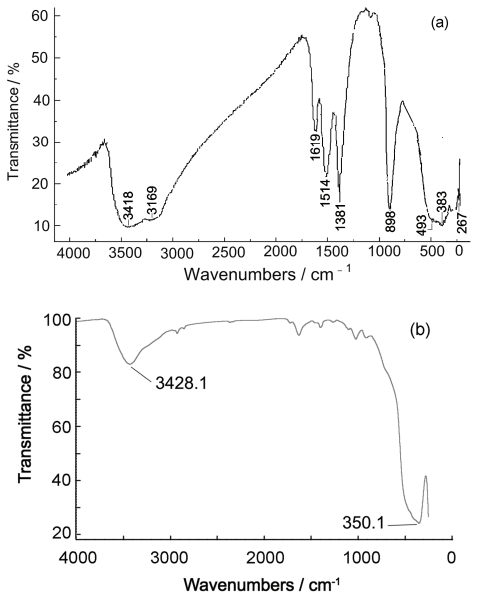

Fig.7 Infrared spectra of uranium powder and the uranium film deposited at 1torr·cm^{-2} with KBr tablet in the vacuum. (a) uranium film, (b) uranium powder.

3.2.2 X-ray EDS

Fig.8 shows the X-ray EDS spectrum of the uranium film deposited at hv = 1253.6 eV, EB =284.6 eV. The film contained just U(65.35%), O (27.38%), C (5.46%) and Pt (1.81%). Carbon is ubiquitous, but the platinum was from the anode wire. Nitrogen, which could be retained as residues from the electrolyte, was not found, indicating that by rinsing the film with a small amount of water no electrolyte was retained.

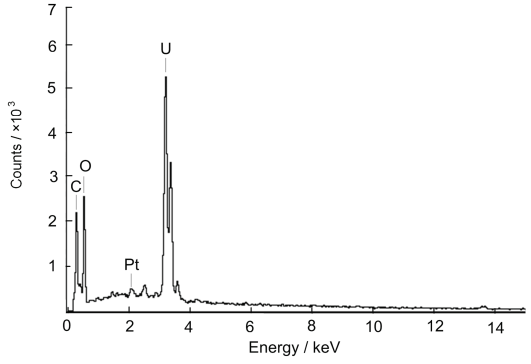

Fig.8 X-ray spectrum of the uranium film deposited at hv = 1253.6 eV and EB=284.6eV.

3.3 Fastness of the uranium films

The samples were placed in organic glass boxes filled with cotton to avoid collision between the films and box walls. The boxes were vibrated for 20 min in the amplitude of about 1.5 mm at 25–80 Hz frequencies, adjusted from minimum to maximum. The film-falling rate is less than 1%.

4 Conclusions

Relatively thick of about 6 mg/cm^2, adherent films of uranium oxide can be deposited on nickel cathode plates following procedures. Avoiding drape and falling off, it is required to control temperature, time, current density, electrolyte concentration, solution acid to get uranium targets with symmetrical layers. Uranium electro-deposition results from the reduction of a starting uranyl salt to a hydrated form of uranium dioxide. The deposition is incidental to water splitting and as such is highly dependent on experimental parameters such as the pH value and concentration of the supporting electrolyte as well as the nature of the cathode surface. The optimized technics are current density at 60–80 mA/cm^2, pH=2–3, temperature at 60°C, and electrolyte concentration at 1.67 mg/mL.

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