DEMONSTRATION EXPERIMENT ON CONTINUOUS URANIUM METAL PRODUCTION SYSTEM BY MOLTEN SALT ELECTROLYSIS

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ABSTRACT

A uranium metal production system from uranium oxides has been developed in order to obtain data for designing pilot plant scale equipment and cost evaluation. An electrolytic apparatus, which can be operated continuously, has been manufactured in 1994 based on the results obtained in a small scale apparatus(1,3). Experiments on the examination of the effects of cathode current density, electrolytic temperature, electrode structure, anode materials and oxidation states of feed on electrolysis behavior such as current efficiency were carried out in the apparatus. The current efficiency through these experiments is over 50%, which is higher value than those reported previously(1,4).

INTRODUCTION

For the purpose of producing uranium metal as a feed material for Atomic Vapor Laser Isotope Separation (AVLIS) which is promising uranium enrichment technology of the next generation, we have been developed a novel technology for the production of uranium metal by molten salt electrolysis which is shown in Figure 1.

Nowadays, as the production process of uranium metal, thermite reduction process of uranium tetra-fluoride (UF₄) with magnesium is conventional(5). However, this process produces large amount of magnesium fluoride (MgF₂) waste contaminated with uranium. The treatment of this radioactive waste makes cost performance worse in Japan. Considering waste minimization and better cost performance, a process such as molten salt electrolysis could be one of hopeful processes for the uranium metal production in the future.

We started the R&D study in 1kg-U/batch electrolytic apparatus in 1989 and have
stepped up to the second phase since 1994, in which electrolytic experiments were carried out in a continuous apparatus newly manufactured. The target concept of apparatus is shown in Figure 2. In this process, liquid uranium metal is directly produced from uranium oxide in the molten fluoride salt bath (BaF$_2$-LiF-UF$_4$) and is transported to casting process to be a desired form for the AVLIS feed. Engineering oriented data concerning cell design, electrode design, anode materials, feed oxide forms, cathode current density and electrolyte temperature were obtained by the experiments.

**EXPERIMENTAL**

**Reagents**

Reagent grade BaF$_2$ and LiF were used, and uranium tetra-fluoride (UF$_4$) was produced by the reaction of uranium dioxide (UO$_2$) with HF at 400°C. These fluoride salts were mixed to be 74wt.%BaF$_2$-11wt.%LiF-15wt.%UF$_4$ and melted before experiment.

Uranium trioxide (UO$_3$) produced by fluidized bed denitration was used as a starting material for making feed oxides (UO$_2$ and U$_3$O$_8$). Uranium dioxide was prepared by reduction of UO$_3$ with hydrogen at 600°C. Triuranium octoxide (U$_3$O$_8$) was produced by calcination under nitrogen atmosphere at 650°C.

**Apparatus**

The schematic view of the apparatus and the summary of its specification are shown in Figure 3 and Table I, respectively. The apparatus consists of five main sections, namely a main body, a heat supply system, a direct current power supply system, an off-gas treatment system and a control system.

The main body consists of a stainless steel vessel, a graphite electrolytic cell, electrode assembly, uranium oxide feed device and molten metal tapping device. The stainless steel vessel can keep inside under Ar gas or vacuum atmosphere according to the experimental procedure. The electrolytic cell is fabricated with a graphite vessel and insulated uranium metal receiver as shown in Figure 4. Two types of electrodes were examined. These are a vertical type and a horizontal type shown in Figures 4(a) and (b). In the horizontal type, four cylindrical studs attached to the uranium metal receiver. The uranium metal receiver acts as a cathode during electrolysis and the cathode surface area is limited to its inside surface in order to keep enough cathode current density for uranium metal deposition. Furthermore, the current concentrate to the studs and deposit uranium metal mainly on this portion. In both types of electrodes, the anode assembly is independently movable in vertical direction. And the anode designs were rods in vertical type (Figure 4(a)) and a slitted block in horizontal type (Figure 4(b)). The graphite cell has a size of 72cm outer diameter and 40cm height, and the capacity of electrolyte is about 50 ℓ (200kg salt). The tapping device has two stopper rods and is able to draw the liquid uranium metal to the molds.

An induction heating method is used in the heat supply system by which the electrolytic cell can be easily heated up to experimental temperature. The direct current power supply system has a maximum capacity of 850A and 20V. The off-gas treatment
Experimental Procedure

The main body was vacuumed below 1 torr, then the electrolytic cell was heated up to 400°C at 2°C/min and then held for 2 hours in order to evacuate volatile materials and moisture, then atmosphere was replaced with Ar gas, and heated up to an experimental temperature at 0.7°C/min. After the electrolyte was melted, the anode assembly was immersed gradually into the electrolyte to the desired position. Electrolysis was started after the temperature of electrolyte was stabilized. The electrolytic current was increased slowly and kept at a prescribed value. The pool level of uranium metal in the receiver was monitored periodically by a level sensor, and was withdrawn into molds by the tapping device when an adequate amount of uranium metal was produced. The electrolysis was continued for about 1,000 minutes in each experimental run.

The experimental conditions are shown in Table II.

RESULTS AND DISCUSSION

From the electrolytic experiments, the followings are determined (1) the function of continuous electrolysis system; (2) the influence of cathode current density on current efficiency; (3) the influence of electrolytic temperature on current efficiency; (4) the possibility of electrode structure modification; (5) the possibility of anode materials modification; (6) the optimization of feed oxide forms. A summary of the electrolytic experiments is shown in Table III.

The function of each system was confirmed in Run 1. It was also checked that every moving part moved smoothly and liquid uranium metal was able to be drawn to the molds quantitatively.

The Influence of Cathode Current Density on Current Efficiency

As the results of Run 2, the current efficiency increased with increasing cathode current density. The current efficiency calculated from uranium metal amount increased from 44% to 53% when cathode current density increased from 1.23 A/cm² to 3.35 A/cm². This tendency was also observed in the former experiment in a small apparatus(2). Furthermore the similar tendency was reported by Piper(6). From these results, the higher cathode current density is desirable. Although the cathode current density higher than 3.35 A/cm² will result in higher current efficiency, it was also observed that the cathode temperature rose. Therefore, it is important to take a countermeasure against increasing of the cathode temperature when the higher cathode current density is adopted.

The Influence of Electrolysis temperature on Current Efficiency

As the results of Run 3, the lower electrolytic temperature resulted in the higher current efficiency. The current efficiency calculated from uranium metal increased from 50% to 55% when electrolytic temperature decreased from 1200°C to 1150°C. This tendency was observed from the electrolytic experiments in our small scale apparatus(2) as well as those reported by Piper(6).
Therefore, lower operating temperature is found to be favorable to higher current efficiency considering difficulties in treating uranium metal at low temperature (melting point of uranium is 1135°C)\(^{(7)}\).

The Possibility of Electrode Structure Modification

According to a comparison of the results of the vertical type electrode with the horizontal type electrode, both average current efficiencies were over 50%. Therefore, with respect to current efficiency, it can be said that there is no difference between vertical and horizontal type electrode.

Considering the pilot plant scale or plant scale apparatus, it is very important that the anode is as simple as possible because it is consumed with electrolysis. Furthermore it is important that easy control of the distance between both electrodes is possible corresponding to the anode consumption. The horizontal type electrolytic cell is simpler in anode and easier in controlling the distance between two electrodes than the vertical one. In the case of horizontal type, the anode is consumed at downside and the distance between electrodes can be controllable only by downward movement of anode.

From above results and consideration, the horizontal type electrode will be the suitable structure in the pilot plant scale or plant scale apparatus.

The Possibility of Anode Materials Modification

In Run5, all experimental conditions are the same as those in Run4 except for the material of anode.

The average current efficiency in Run5 was 54%, which was equal to that in Run4. The analytical results about impurity of graphite anode, carbon anode and uranium metal ingot are shown in Table IV. The impurities of uranium are reasonably low, though the impurity level is higher in the case of carbon than the case of graphite. Cell voltage showed slightly higher value in Run5, which might be caused by electrical resistance between carbon anode and anode connector. But the electrical resistance is thought to be caused by the difficulty in machining of carbon at the connecting portion and such electrical resistance could be easily reduced by improving the connection using conductive binder or glue.

From the results and especially considering carbon is more economical material than graphite, the carbon anode is practical in the plant scale apparatus.

The Optimization of Feed Oxide Forms

In the Run6, the average current efficiency 52% was obtained and this value was almost the same as that in Run4.

Some test pieces made of graphite with the same grade of electrolytic cell were set into the apparatus during the experiments, and their weight changes before and after the experiments were compared. The result of this comparison is shown in Figure 5. In the case of test piece placed out of the electrolyte, the amount of consumption caused by $\text{U}_3\text{O}_8$ feed was larger than that caused by $\text{UO}_2$. On the other hand, in the case of test piece placed in the electrolyte, any notable consumption was not observed in both the cases of $\text{U}_3\text{O}_8$ and $\text{UO}_2$. Undesirable consumption which will shorten the life of electrolytic cell was observed in the $\text{U}_3\text{O}_8$ case. Therefore, $\text{UO}_2$ would be preferable to
**CONCLUSION**

In the experiments using the continuous apparatus, a current efficiency over 50% was obtained constantly, and stable electrolysis was possible under the following conditions: (1) electrolytic temperature between 1150°C and 1200°C, (2) cathode current density between 1.3A/cm² and 3.4A/cm², (3) both of vertical and horizontal type electrode structures, (4) both of graphite and carbon anodes and (5) both of UO₂ and U₃O₈ for feed materials (consumption of cell material was observed in the U₃O₈ case).

The more desirable conditions are, (1) the electrolytic temperature is 1150°C, (2) the cathode current density is over 3.4A/cm², (3) the electrode structure is horizontal type, (4) the anode material is carbon and (5) the feed material is UO₂.

These results will be used for design and cost evaluation of the pilot plant scale apparatus for uranium metal production by molten salt electrolysis.

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Figure 1  A Process Flow of Uranium Metal Production

Figure 2  A Future Conceptual Drawing of Apparatus for Uranium Metal Production
Figure 3 A Schematic Diagram of the Electrolytic Apparatus

Table I Summary of the Apparatus Specification

| Component of Main Body         | Vertical Type | Horizontal Type          |
|--------------------------------|---------------|--------------------------|
| Normal Temperature             | 1200 °C       |                          |
| Heat Supply                    | Inducting Heating |                      |
| Direct Current Power Supply    | 850A, 20V (maximum value) |              |
| Electrolyte                    | BaF$_2$ - LiF - UF$_4$ (74-11-15 wt.%) , 180kg     |
| Component of Main Body         | Stainless Steel Vessel (1700mm × 2150mm) | Graphite Electrolytic Cell (720mm$^{OD}$ × 620mm$^{ID}$) |
| Graphite Rod Anode             | (50mm $\phi$ × 8) | Graphite or Carbon Block Anode (260mm $\phi$ × 80mm$^{H1}$) |
| Tungsten Rod Cathode           | (30mm $\phi$) | Graphite Stud Cathode (20mm $\phi$ × 4) |
| Off-Gas Treatment             | Filters for salt vapor trap, NaF Trap, Burner for CO gas |
Figure 4(a) Electrolytic Cell; Vertical Type

Figure 4(b) Electrolytic Cell; Horizontal Type
Table II Experimental Condition

| Temperature of Electrolyte (°C) | Run1  | Run2  | Run3  | Run4  | Run5  | Run6  |
|---------------------------------|-------|-------|-------|-------|-------|-------|
|                                 | 1200  | 1200  | 1150  | 1175  | 1200  | 1200  |
| Direct Current (A)              | 500   | 300   | 500   | 500   | 500   | 500   |
| Anode Current Density (A/cm²)   | 0.59  | 0.35  | 0.59  | 0.88  | 0.59  | 0.27  |
| Cathode Current Density (A/cm²) | 2.23  | 1.34  | 2.23  | 3.35  | 2.23  | 0.65~1.55 |
| Electrode Structure             | Vertical | Vertical | Vertical | Horizontal | Horizontal | Horizontal |
| Anode Material                  | Graphite | Graphite | Graphite | Graphite | Carbon | Graphite |
| Feed Material                   | UO₂    | UO₂    | UO₂    | UO₂    | UO₂    | U₂O₅ |

Table III Summary of Electrolytic Experiments

| Cell Voltage (V)                | Run 1   | Run 2   | Run 3   | Run 4   | Run 5   | Run 6   |
|---------------------------------|---------|---------|---------|---------|---------|---------|
|                                 | 6.8~7.5 | 5.0~9.0 | 6.8~7.4 | 6.3~6.8 | 6.8~7.8 | 6.3~7.2 |
| Current Efficiency (%)          | 52      | 44 (1.34 A/cm²) | 55 (1150°C) | 52 (1175°C) | 50 (1200°C) | 54      | 54      | 52      |
| Influence of Electrode Structure| —       | —       | —       | —       | —       | —       | —       | —       | —       |
| Influence of Anode Material     | —       | —       | —       | —       | —       | —       | —       | —       | —       |
| Influence of Feed Material      | —       | —       | —       | —       | —       | —       | —       | Graphite consumption was observed |
### Table IV Analytical Results about Impurities of Graphite Anode, Carbon Anode and Uranium Metal Ingot

| Elements  | Impurities (ppm) | Graphite Anode | Carbon Anode | Uranium Ingot | AVLIS (Specification of MMES*) |
|----------|------------------|----------------|--------------|---------------|-------------------------------|
|          |                  |                |              |               |                               |
| B        | 1.5              | 3.6            | 1.7          | <50           |                               |
| Ca       | 8.7              | 38             | <5           | <50           |                               |
| Cu       | <0.08            | 0.9            | <1           | <200          |                               |
| Fe       | 0.22             | 210            | 31           | <200          |                               |
| Mg       | <0.02            | 10             | <1           | <50           |                               |
| Mn       | <0.08            | 2.4            | 1            | <50           |                               |
| Na       | 0.05             | 6.2            | <1           | <50           |                               |
| Si       | 1.3              | 360            | <10          | <100          |                               |

*Reference (8)

**Figure 5 The Amount of Consumption of Test Piece**