DEMONSTRATION EXPERIMENT OF URANIUM METAL PRODUCTION SYSTEM

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ABSTRACT

Demonstration experiments of uranium metal production system have been carried out in order to verify its technical feasibility. Uranium metal is produced from its oxides by molten salt electrolysis and continuously cast into an uranium ingot by Vacuum Melting and Pressurized Upward Continuous Casting (VMCC) method. Current efficiency of electrolysis was around 50%, which was higher value than those reported in earlier experiments. A rod of uranium metal, which is 80 cm in length and 1 cm in diameter, was obtained with high purity (>99.7%) through the production system. Major impurities in the metal were B, C, Cr, Fe, Mn, Mo, Ni, O and W, which are from its oxide raw material, cell materials and salt impurities.

INTRODUCTION

The atomic vapor laser isotope separation (AVLIS) will be a promising uranium enrichment technology for the next generation because of its high cost performance and high enrichment efficiency. In this AVLIS enrichment process, uranium metal or uranium metal alloy will be used as feed material. Today, commercial production of uranium metal in the world is done by thermite reduction of UF$_4$ with magnesium (1). In this thermite process, large amount of MgF$_2$ contaminated with uranium is produced as a byproduct simultaneously.

Considering cost performance, minimization of waste production and continuous process concept, an electrolytic process for producing uranium metal directly from uranium oxide will offer potential advantages over the existing commercial process (2).

Metal Mining Agency of Japan has carried out a feasibility study on metallic uranium production systems for AVLIS feed materials since fiscal 1989. In this study, uranium metal
production from uranium oxide by molten salt electrolysis has been examined to get basic characteristics of electrolysis and design data for scale-up (3, 4), and system component technologies such as molten salts electrolysis for uranium metal production and continuous casting have been developed.

**Process Concept**

A process flow sheet of uranium metal production and a future concept of apparatus is shown in Fig.1 and Fig.2, respectively. Uranium oxide (UO$_2$) was directly reduced into uranium metal by electrolysis in molten fluoride melts. The molten uranium metal is transferred to VMCC stage, and cast into a uranium ingot (Rod). In this conceptual process, uranium oxide will be directly converted into uranium metal rod. In this study, however, electrolysis and casting experiments were carried out separately to confirm its technical feasibility.

**EXPERIMENT**

**Electrolysis**

*Reagent* - Mixture of BaF$_2$, LiF and UF$_4$ salts was used as electrolyte. Its composition was BaF$_2$-LiF-UF$_4$ (74-11-15 wt.%). Uranium tetrafluoride acts as solvent for uranium oxide in this electrolysis. Lithium fluoride acts to increase the electrical conductivity of electrolyte. These salts were reagent grade chemicals. Uranium tetrafluoride was produced by a reaction of UO$_2$ with HF at about 400°C. These fluorides were mixed and premelted before experiment. In most cases, UO$_3$ produced by fluidized bed denitration was used as starting material. Uranium trioxide was also treated in a vacuum furnace to remove remaining acidic moisture at 450°C. Triuranium octoxide (U$_3$O$_8$) was prepared by calcination of UO$_3$ in the N$_2$ atmosphere at 650°C. Uranium dioxide was prepared by reduction of UO$_3$ with hydrogen at 600°C.

**Apparatus** - A schematic feature of an electrolytic apparatus and an outline of the apparatus are shown in Fig.3 and Table 1, respectively. The electrolytic cell made of graphite has a size of 20 cm inner diameter and 35 cm in height. The present cell concept is a neutral hearth with a rod type cathode, which is different from the Hall process. The anode is made of graphite which has a cylindrical shape with slits as a standard case. The cathode rod is made of tungsten. It is considered to act as uranium electrode under electrolysis because the tungsten surface is covered with liquid uranium. A graphite uranium metal receiver covered with boron nitride has a capacity for 3 kg uranium metal and is set just below the cathode. The electrolytic cell is enclosed in a quartz tube with steel flanges so that a gas tight enclosure was achieved. Argon gas with high purity is used as purge gas in the cell. Off gas is introduced to gas mass spectrometer (UTI Instruments Co., ISS-325A), for the measurement of gas components such as CO, CO$_2$ and CF$_4$ with electrolysis. Direct current generator for electrolysis has a capacity of 0~20V and 0~500A. Induction heating which has a maximum heating capacity of 1400°C (Fujidenpa Kogyo Co. Ltd., 440V-50Hz, 3-Phase, 280 kVA) is used to bring the cell to the experiment temperature of about 1200°C and maintain it during the experiment.
**Procedure** - Mixture of LiF, BaF₂ and UF₄ was pretreated in a vacuum at 400°C and in Ar at 800°C for 30 minutes in order to evacuate volatile species and moisture, then heated up to about 1200°C, which is well over the melting point of LiF-BaF₂-UF₄ electrolyte and the melting point of uranium metal (1132°C). The electrodes and uranium receiver assembly were immersed slowly into the electrolyte to a desired depth. All of the experiments were carried out by constant current mode. Before melting, all of the uranium oxides were fed into the cell. And off-gas composition was analyzed continuously with electrolysis. Direct current, cell voltage, temperature, and induction heating power were also recorded continuously. After electrolysis, cathode and anode electrodes assembly, and uranium metal receiver were removed upward in order to minimize back-reaction of the metal with the electrolyte. After cooling, uranium metal was removed from the receiver and was weighed. Electrolysis experiments were repeated 5 times in an optimum condition in order to confirm its reproducibility.

**Uranium Metal Rod Production**

In order to confirm the production of uranium metal rod by continuous casting and to minimize the scrap of uranium metal, an availability of Vacuum Melting and Pressurized Upward Continuous Casting (VMCC) method was examined. A summary of the experimental conditions is listed in Table 2.

**Uranium Material** - The uranium metal produced by electrolysis mentioned above is used for this casting experiment. In order to remove the salts on the metal, the uranium metal was immersed in nitric acid (reagent grade) and rinsed by both distilled water and acetone (reagent grade).

**Apparatus** - A schematic diagram of VMCC experimental apparatus is shown Fig. 4. The containment vessel is made of stainless steel and has a size of 120cm I.D. and 120cm in height, and a total volume is 1.1m³. The inner wall of the cell is cooled by water. The cell is enclosed so tightly that air contamination cannot be brought into the cell. First, the air in the tank is degassed by a oil-diffusion pump, and the pressure can be achieved $1 \times 10^{-5}$ Torr within 60 minutes. Then, the cell is filled with high purity Ar gas (>99.999%). A crucible for melting uranium made of graphite has a size of 15cm inner diameter and 18cm in height. This graphite crucible is heated by induction heating (Max. 60kW, 1500°C). A nozzle is attached to a copper jacket cooled by water in order to cast molten uranium metal into a rod.

**Procedure** - Initially, uranium metal (~16 kg) was charged into the graphite crucible. The cell was enclosed. Under a pressure of $1 \times 10^{-4}$ Torr, the metal was heated up to a temperature of about 100~200°C higher than the melting point of U (1132°C). Keeping a vacuum under $3 \times 10^{-4}$ Torr for a couple of hours, salt impurities such as Ba, F and Li volatile during this period. And then Ar gas of high purity was purged into the cell up to a pressure of $2.5 \times 10^{5}$ Pa. A tip of the nozzle was dipped into molten uranium bath, and a cylindrical rod was cast upward continuously.
RESULTS AND DISCUSSION

Electrolysis

_Uranium Metal_ - Five electrolytic experiments were carried out. The typical cell voltage and current chart are shown in Fig. 5. A summary of the results are listed in Table 3. Uranium metal was obtained in three forms of "ingot", "shot" and "powder". Considering this uranium is transferred to the casting experiments, it is better to produce uranium metal as an "ingot". Thus, experimental conditions were optimized to produce this required metal, as well as to achieve higher current efficiency. Except for Test 1, more than 1kg uranium metal were produced as aggregate form.

In this electrolysis process, uranium ion was reduced to uranium metal on the surface of the tungsten cathode, and liquid uranium metal will flow downward into the graphite crucible under the cathode. And then uranium metal was coalesced making "metal pool" in the crucible. In our experiments, metal coalescence tends to become poorer with higher oxide ion (O^{2-}) concentration in the melts.

_Off-Gas Analysis_ - During electrolysis off-gas from the cell was introduced to the gas mass spectrometer, and the concentrations of CO, CO_2 and CF_4 gas were analyzed. The typical off gas (CO, CO_2 and CF_4) chart data is shown in Fig. 6.

During electrolysis, CO, CO_2 and CF_4 gas were continuously detected. In addition to the oxidation of O^{2-} in the melts, F^- were simultaneously oxidized at the surface of the anodes. Though CF_4 gas was evolved, a sudden increase in cell voltage such as "anode effect" was not observed all through the experiments.

_Current Efficiency_ - Current efficiencies of each experiment were calculated by the off-gas volume of CO, CO_2 and CF_4, and by weight of uranium metal produced. From Test 2 to Test 5, both of the CE values are consistent and around 50%. These values seem to be higher compared with other electrolytic oxide processes. However, these relatively low values might be attributed to several side reactions such as;

\[ \text{U} + 3\text{UF}_4 \rightarrow 4\text{UF}_3 \]  \[1\]

\[ \text{U} + 2\text{CO} \rightarrow \text{UO}_2 + 2\text{C} \]  \[2\]

_Uranium Metal Rod Production_

To confirm the reliability of the apparatus and the reproducibility of the casting, five casting experiments are conducted. In all tests, uranium metal were cast in a form of a rod (49~80cm in length, 1cm-O.D.). The length of the rod was restricted by a usable uranium metal weight. The defects in the rods were not observed. But it is necessary to improve the surface of the rod and the casting speed. Through five tests, there was not observed any operational problem. The casting conditions and the results are summarized in Table 4.

_Implurities Behavior in the Process_

Impurities in each uranium formed in this process are analyzed and shown in Table 5.
These analyzed values were deviated depending on sampling points.

Uranium metal rods in the final product have impurities such as B, C, Cr, Fe, Mn, Mo, Ni, O and W.

It was found that B, Mo and W in the uranium metal were from cell assembly materials such as BN insulator, Mo rod, W cathode and Mo induction insulation sheet. And Cr, Fe, Mn and Ti which were impurities in uranium oxide were reduced and condensed in the uranium metal. Na, Ca and P were not transferred to the metal and remained in the electrolyte. Ba, Li and F were contaminants from the salt and were easily separated by volatilization or mechanical settlement of liquid.

After melted in vacuum atmosphere and cast, it appeared that the concentration of volatile species such as Ba, C, F, N, Na, Li and O decreased but that heavy metals such as Cr, Fe, Mo and W still remained in uranium metal.

CONCLUSION

Demonstration experiments of uranium metal production system has been carried out. Uranium metal was produced from its oxides by molten salt electrolysis and cast into an uranium ingot by Vacuum Melting and Pressurized Upward Continuous Casting (VMCC) method. For the electrolysis, current efficiency obtained was around 50%, which was higher value than reported in earlier experiments. A rod of uranium metal, which is 80 cm in length and 1cm in diameter, was produced with high purity (>99.7%). The origination of the impurities contained in the metal such as B, C, Cr, Fe, Mn, Mo, Ni, O and W were identified.

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Fig. 1 A Process Flow of Uranium Metal Production.

Fig. 2 A Future Concept of Apparatus.

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Table 1  Typical Operating Data for Electrolytic Reduction of Uranium Oxides to Uranium Metal.

| Cell size       | 20cm ID × 33cm high |
|-----------------|---------------------|
| Electrolyte     | BaF$_2$-LiF$_2$-UF$_4$ (74-11-15 wt.%) |
| Temperature     | 1150°C |
| Anode type      | Graphite |
| Anode shape     | Rods |
| Cathode type    | Tungsten rod |
| Current         | 200 A |
| Anode current density | 0.635-0.667 A/cm$^2$ |
| Cathode current density | 2.05-2.31 A/cm$^2$ |
| Feed material   | UO$_2$ |
| Uranium metal   | Graphite crucible |
| receiver        | surrounded with BN insulation |
| Heating         | Induction coil heating |

Table 2  A summary of the experimental conditions (VMCC)

| Cell Size      | 120cm-OD × 120 cm High |
|----------------|------------------------|
| Cell Volume    | 1.1 m$^3$ |
| Uranium Charged| 14-20 kg/Batch |
| Crucible       | Graphite |
| (15 cm-ID × 18 cm high) |
| Nozzle         | Graphite or Y$_2$O$_3$ |
| Heating        | Induction Heating |
| Temperature    | 1250-1350 °C |
| Pressure       | 1.5-2.5 × 10$^5$ Pa |
| Casting Speed  | 3-30 mm/min |
| Cast Rod Shape | Cylindrical |
| Rod Size       | 10 mm-OD |

Fig. 3  Schematic Diagram of Electrolytic Experimental Apparatus.

Fig. 4  A schematic diagram of VMCC experimental apparatus.
Fig. 5 The typical cell voltage and current chart during electrolysis. (Test 4)

Fig. 6 The typical off gas (CO, CO₂ and CF₄ gases) chart during electrolysis. (Test 4)

Table 3 Summary of the Electrolytic Experiments.

| Test  | Temperature of electrolyte | Anode Current Density | Cathode Current Density | Cell Voltage | U (ingot) | U (shot) | U (powder) | CE (Calculated by metal weighed) | CE (Calculated by off-gas volume) |
|-------|----------------------------|-----------------------|------------------------|--------------|-----------|----------|------------|-------------------------------|----------------------------------|
| 1     | 1110-1152°C                | 0.635 A/cm²          | 2.05 A/cm²             | 3.59-4.21 V  | 197 g     | 251 g    | 245 g      | 44%                           | 64%                              |
| 2     | 1104-1153°C                | 0.667 A/cm²          | 2.14 A/cm²             | 3.95-4.36 V  | 1082 g    | 63 g     | 47 g       | 53%                           | 52%                              |
| 3     | 1103-1186°C                | 0.667 A/cm²          | 2.31 A/cm²             | 3.93-4.38 V  | 1231 g    | 51 g     | 47 g       | 50%                           | 50%                              |
| 4     | 1101-1153°C                | 0.667 A/cm²          | 2.31 A/cm²             | 4.19-4.58 V  | 1295 g    | 67 g     | 34 g       | 52%                           | 49%                              |
| 5     | 1097-1152°C                | 0.667 A/cm²          | 2.31 A/cm²             | 3.81-4.45 V  | 1253 g    | 75 g     | 42 g       | 51%                           | 48%                              |

Table 4 The casting conditions and the results.

| Test  | Pressure       | Temperature | Casting Speed | Cast Rod Size | Crack | Inside Defect |
|-------|----------------|-------------|---------------|---------------|-------|---------------|
| 1     | 2.5 × 10⁵ Pa   | 1336-1340°C | 8 mm/min      | 1 cm OD × 80 cm L | Some | None          |
| 2     | 2.5 × 10⁵ Pa   | 1361-1368°C | 8 mm/min      | 1 cm OD × 54 cm L | Some | None          |
| 3     | 2.5 × 10⁵ Pa   | 1363-1367°C | 8 mm/min      | 1 cm OD × 49 cm L | Some | None          |
| 4     | 2.5 × 10⁵ Pa   | 1354-1362°C | 8 mm/min      | 1 cm OD × 59 cm L | Some | None          |
| 5     | 2.5 × 10⁵ Pa   | 1355-1358°C | 8 mm/min      | 1 cm OD × 61 cm L | Some | None          |
Table 5. Analytical Results of Impurities of Uranium Oxide, Fluoride Salts, Uranium Metal and Uranium Ingot.

| Impurities Elements | UO₂ as Feed Material | Salts before Electrolysis | Metal U (5 Tests Averaged) | Salts after Electrolysis | U ingot by VMCC |
|---------------------|----------------------|---------------------------|-----------------------------|--------------------------|-----------------|
|                     |                      |                           |                             |                          |                 |
| Ag                  | <2                   | <2                        | <2                          | <2                       | 2               |
| B                   | <0.4                 | 1                         | 164                         | <0.4                     | 100             |
| Ba                  | <2                   | -                         | 1830                        | -                        | 2               |
| Be                  | <2                   | <2                        | <2                          | <2                       | <2              |
| Bi                  | 1                    | 1                         | 15                          | 150                      | 2               |
| Ca                  | <5                   | <5                        | 9                           | 33                       | 5               |
| Cd                  | <0.4                 | <0.4                      | <0.4                        | <0.4                     | <0.4            |
| Co                  | <2                   | <2                        | <2                          | <2                       | <2              |
| Cr                  | <5                   | <5                        | 15                          | 5                        | 150             |
| Cu                  | 1                    | 1                         | 2                           | 1                        | 3               |
| Fe                  | 15                   | 20                        | 244                         | 10                       | 300             |
| In                  | <1                   | <1                        | <1                          | <1                       | <1              |
| Li                  | <2                   | -                         | 108                         | -                        | 2               |
| Mg                  | <1                   | <1                        | <1                          | <1                       | <1              |
| Mn                  | <1                   | <1                        | 11                          | 1                        | 22              |
| Mo                  | 1                    | >4000                     | >4000                        | 290                      | 1100            |
| Na                  | <1                   | 87                        | 3                           | 240                      | <1              |
| Ni                  | <5                   | <5                        | 5                           | <5                       | 26              |
| P                   | <50                  | 2200                      | 50                          | 7000                     | <50             |
| Pb                  | <1                   | <1                        | <1                          | <1                       | <1              |
| Si                  | <10                  | <10                       | 13                          | <10                      | 10              |
| Sn                  | <1                   | <1                        | <1                          | <1                       | <1              |
| Ti                  | <4                   | 9                         | 25                          | <4                       | 6               |
| V                   | <1                   | 1                         | 5                           | <1                       | 1               |
| W                   | <50                  | <50                       | 170                         | <50                      | 400             |
| Zn                  | <10                  | <10                       | <10                         | <10                      | <10             |
| C                   | -                    | -                         | 777                         | -                        | 279             |
| N                   | -                    | -                         | 33                          | -                        | 3               |
| O                   | -                    | -                         | 807                         | -                        | 141             |
| F                   | 400                  | -                         | 584                         | -                        | 5               |

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