Electrorefining of Zircaloy-4 in LiCl-KCl to Decontmatinate Irradiated Cladding – 16238

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ABSTRACT

Electrorefining on unirradiated Zircaloy-4 specimen in LiCl-KCl was performed by managing the anode potential to identify whether high purity zirconium can be recovered in metallic form by electrorefining. Four different concentrations of $ZrCl_4$ (0.1, 0.5, 1.0 and 2.0 wt%) were tested. Results indicate that high purity metallic zirconium was recovered at low concentration of $ZrCl_4$ but ZrCl could be recovered at high concentration. The electrorefining experiments were simulated by a three-dimensional computational electrorefining model. Several physical properties were tested, and a set of physical properties was determined in the condition where chemical forms of cathode deposits estimated by the computational model accorded with the experimental results. Using those properties, codeposition of zirconium and uranium was simulated in the geometry of a preliminary designed electrorefiner for irradiated Zircaloy claddings. Operating conditions that can lead to the formation of zirconium metal without ZrCl and uranium were calculated.

INTRODUCTION

A large amount of radioactive zirconium alloy waste is inevitable during nuclear reactor operation because zirconium alloy claddings constitute 40 wt% volume of the nuclear fuel assembly of a pressurized water reactor (PWR). Zircaloy-4 cladding irradiated in a PWR is classified as the intermediate level waste in both the radioactive waste classification of IAEA and that of Republic of Korea since long-living actinide elements and fission products can penetrate into the cladding [1]. However, radioactivity of zirconium radioisotopes such as Zr-93 in the used nuclear fuel cladding is not as significant as actinides and fission products. If zirconium can be separated from the irradiated cladding, the final radioactive waste volume in an intermediate level waste repository can be greatly reduced. In addition, the recovered zirconium could be recycled for reutilization in nuclear industry such as a constituent of an U-TRU-Zr metallic fuel for fast reactor.

Electrorefining can be a promising option for effectively separating high purity zirconium from the irradiated cladding as it has been utilized for recovering uranium from used nuclear fuel. Since chlorides salts have advantages of low melting temperature and corrosion risk compared to fluoride salts, LiCl-KCl was utilized for electrorefining experiments in this study. This paper describes results on lab-scale electrorefining experiments of unirradiated Zircaloy-4 specimens in LiCl-KCl, computational modeling on the electrorefining experiments and preliminary

simulation for electrorefining of irradiated cladding.

ELECTROREFINING EXPERIMENT

Lab-scale electrorefining of unirradiated Zircaloy-4 specimen was conducted for about 5 to 6 hours at four different concentrations of $ZrCl_4$ (0.1, 0.5, 1.0 and 2.0 wt%) at 500°C. Since major elements of Zircaloy-4 excluding Zr (Sn, Cr and Fe) are more reductive than Zr, anode potential was managed at about -0.9 V (1 wt% Ag/AgCl) so as to suppress dissolution of those elements. Chemical form and composition of deposits after electrorefining were analyzed by X-ray diffraction (XRD) and inductively coupled plasma mass spectrometry (ICP-MS) respectively.

Experimental setup

Electrorefining experiments was performed in a glove box under argon atmosphere with oxygen and moisture concentration less than 0.1 ppm. Well type furnace equipped at the bottom of the glove box was utilized to keep temperature of the electrorefining cell as 500±1°C. Electrorefining cell was prepared as represented in Fig. 1. Quartz tube with an inner diameter of 27 mm, an outer diameter of 30 mm and a height of 380 mm was utilized for a molten salt container. Tungsten rod with a diameter of 3.175 mm and purity of 99.95% was used for a cathode. Anode basket was made of 316 stainless steel with each side of 10 mm and height of 30 mm. The reference electrode was a 1 wt. % Ag/AgCl electrode. Temperature of molten salts was measured directly in the electrorefining cell using a k-type thermocouple. Mixture of anhydrous LiCl-KCl salts with purity of 99.99% and anhydrous $ZrCl_4$ with purity of 99.99% was used as electrolyte. Six Zircaloy-4 cuts having size of about 5 x 10 x 2 mm were loaded into the anode basket.
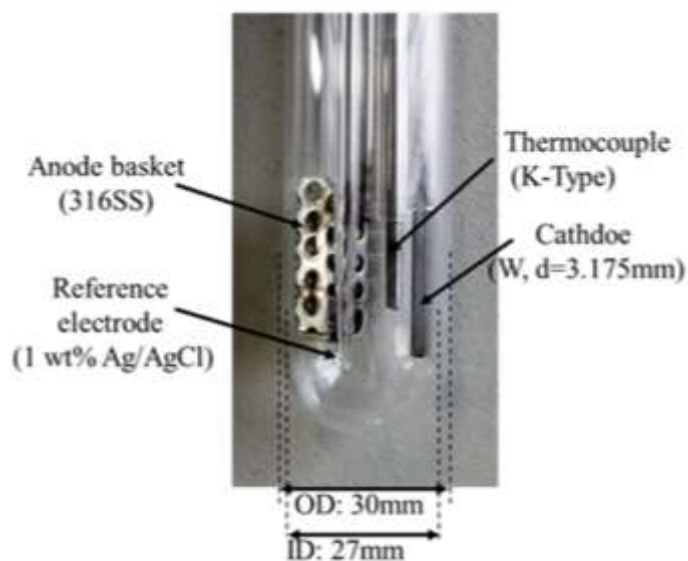

Fig. 1. Lab-scale Zircaloy-4 electrorefining cell

Results and discussion

The specimen used for the electrorefining experiments was mainly composed of Zr of 98.6 wt% and there were also Sn of 1.104 wt%, Cr of 0.083 wt% and Fe of 0.160 wt% as major elements. After all electrorefining experiments, cathode deposits were powdery regardless of $ZrCl_4$ concentration, and they were easily detached from the cathode. The cathode deposits contained some amount of LiCl-KCl salts, but the cathode deposits except the trapped LiCl-KCl consisted of almost 100 % Zr in all electrorefining experiments. Concentrations of Sn, Cr and Fe in the cathode deposits were below the detection limits of ICP-MS. Chemical forms of cathode deposits were investigated by XRD. When concentration of $ZrCl_4$ was low as 0.1 and 0.5 wt%, chemical form of the cathode deposits was not ZrCl but Zr metal. On the other hand, in the case of 2.0 wt% $ZrCl_4$, ZrCl was recovered from the cathode deposits without Zr metal. After the electrorefining at the $ZrCl_4$ concentration of 1 wt%, both Zr metal and ZrCl were observed. Therefore, low concentration would be advantageous to recover high purity metallic zirconium from the used nuclear fuel cladding.

TABLE I. Chemical form and composition of the cathode deposits after lab-scale Zircaloy-4 electrorefining

$ZrCl_4$ concentration in the initial molten salts (wt%)		0.1	0.5	1.0	2.0
Chemical form of deposits		Zr	Zr	Zr + ZrCl	ZrCl
Composition of deposits[a] (wt%)	Zr	Over 99.999	Over 99.999	Over 99.999	Over 99.999
	Sn	N/A	N/A	N/A	N/A
	Fe	N/A	N/A	N/A	N/A
	Cr	N/A	N/A	N/A	N/A

a   Molten salts trapped in the deposits are excluded when calculating compositions.

After electrorefining in the salts containing $ZrCl_4$ of 0.1, 0.5 and 1.0 wt%, black powders were observed in the bottom of molten salts. These powders were investigated by XRD and it was revealed that chemical forms of these powders are equivalent to those of cathode deposits for each concentration. After electrorefining in the salts of 2.0 wt% $ZrCl_4$, black powders were not shown at the bottom of the salts. In addition, the amount of the deposits at those concentration was less than the deposits at 2.0 wt% even though more electric charges were passed at those concentrations. Therefore, it would mean that black powders found at the bottom had been detached from the cathode during the electrorefining. Color of molten salts after electrorefining became darker from light brown to dark brown as $ZrCl_4$ concentration increases, and this would indicate that Zr^{2+} is easily produced at high concentration of $ZrCl_4$.

BENCHMARK OF ELECTROREFINING EXPERIMENTS

A three-dimensional electrochemo-hydrodynamic computational model based on a conventional fluid dynamics code, ANSYS-CFX by Seoul National University [2, 3] was used. The simulation of the Zircaloy-4 electrorefining experiments was performed in the geometry represented in Fig. 2 by the computational model with multi-step reduction of Zr^{4+} as follows:

$$Zr^{4+}+3e^{-}+Cl^{-}\rightarrow ZrCl$$

$$ZrCl+e^{-}\rightarrow Zr+Cl^{-}.$$

Anode basket
(316SS)

Thermocouple
(K-Type)

Cathdoe
(W, d=3.175mm)

Reference
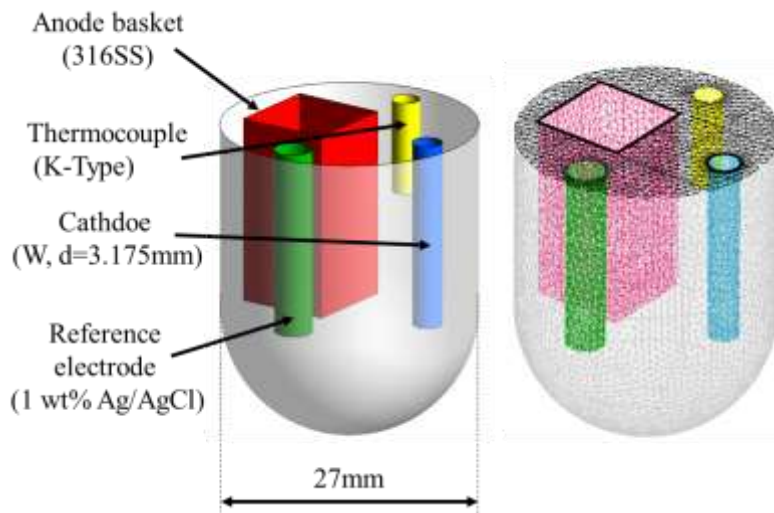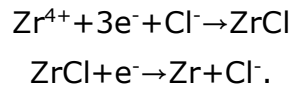electrode
(1 wt% Ag/AgCl)

27mm

Fig. 2. Geometry and mesh grid used for the computational modeling of the lab-scale Zircaloy-4 electrorefining

Since rate constants for the upper reactions have been seldom found in the previous studies, rate constant for the reaction between Zr^{4+} and ZrCl was assumed as the value of the redox reaction between U^{3+} and U, $1.69X10^{-4}$ m/s, and several values from $1X10^{-6}$ to $X10^{-1}$ were tested for the rate constant of the reaction between ZrCl and Zr [4]. In addition, assumption of steady state was introduced to simplify the calculation. Weight ratios of Zr metal in the cathode deposits were calculated, and they are compared to the experimental results quantitatively.

Mathematical model

The mole production rate of ZrCl from Zr^{4+}, $\dot{m}_{p,ZrCl}$ can be determined by combining the Butler-Volmer equation (Eq. 1) and the Fick's first law (Eq. 2) as follows:

$$\dot{m}_{p,ZrCl} = -\frac{i_{ZrCl}}{n_{ZrCl}F}$$

$$= -k_{0,ZrCl}[-C_{Zr^{4+}}(0,t)\exp(-\alpha_{ZrCl}\frac{n_{ZrCl}F}{RT}(E-E_{ZrCl}^{0'})) \quad \text{(Eq. 1)}$$

$$+ \exp((1-\alpha_{ZrCl})\frac{n_{ZrCl}F}{RT}(E-E_{ZrCl}^{0'}))]$$

$$J_{Zr^{4+}} = D_{Zr^{4+}}\frac{C_{b,Zr^{4+}}-C_{Zr^{4+}}(0,t)}{\delta} = \dot{m}_{c,Zr^{4+}} = \dot{m}_{p,ZrCl} \quad \text{(Eq. 2)}$$

$$i_{ZrCl} = \frac{n_{ZrCl}Fk_{0,ZrCl}[-C_{Zr^{4+}}(0,t)\exp(-\alpha_{ZrCl}\frac{n_{ZrCl}F}{RT}(E-E_{ZrCl}^{0'})) \\ + \exp((1-\alpha_{ZrCl})\frac{n_{ZrCl}F}{RT}(E-E_{ZrCl}^{0'}))]}{1+\frac{\delta k_{0,ZrCl}}{D_{Zr^{4+}}}\exp(-\alpha_{ZrCl}\frac{n_{ZrCl}F}{RT}(E-E_{ZrCl}^{0'}))} \quad \text{(Eq. 3)}$$

where i_{ZrCl} is the current density used for the reduction of Zr^{4+} into ZrCl, n_i is the number of electron participating in the reaction producing species i, F is the Faraday constant (96485 C/mol), $k_{0,i}$ is the rate constant for the reaction producing species i, $C_i(0,t)$ is the surface concentration of species i on the electrode, α_i is the transfer coefficient for the reaction producing species i, R is the universal gas constant constant (8.314 J/K/mol), T is the temperature, E is the electrode potential, $E_i^{0'}$ is the formal potential for the reaction producing species i, J_i is the flux density of species i, D_i is the diffusion coefficient of species i, $C_{b,i}$ is the bulk concentration of species i , δ is the diffusion boundary layer thickness and $\dot{m}_{c,Zr^{4+}}$ is the mole consumption rate of Zr^{4+} by the reaction consuming Zr^{4+}. The mole production rate of Zr metal from ZrCl, $\dot{m}_{p,Zr}$ could be expressed by the Butler-Volmer equation:

$$\dot{m}_{p,Zr} = \frac{i_{Zr}}{n_{Zr}F}$$
$$= k_{0,Zr}[-\exp(-\alpha_{Zr}\frac{n_{Zr}F}{RT}(E-E_{Zr}^{0'}))+\exp((1-\alpha_{Zr})\frac{n_{Zr}F}{RT}(E-E_{Zr}^{0'}))]=\dot{m}_{c,ZrCl} \quad \text{(Eq. 4)}$$

where $\dot{m}_{c,ZrCl}$ is the mole consumption rate of ZrCl by the reaction consuming ZrCl. The net mole production rate of ZrCl can be determined by subtracting the mole consumption rate of ZrCl from the production rate.

However, as represented in Eq. 4, the current density for the reduction of ZrCl into Zr does not have Zr(IV) concentration dependency. Therefore, the current would increase infinitely in negative direction as applied potential becomes more negative unless restriction is applied to Eq. 4. If so, below a certain electrode potential, the mole consumption rate of ZrCl resulting from the reduction of ZrCl will be larger than the mole production rate of ZrCl from the reduction of Zr^{4+}. Therefore, a restriction for Eq. 4 was established. When the mole consumption rate of ZrCl calculated by Eq. 4 is higher than the mole production rate of ZrCl calculated by Eq. 3, the restriction that the mole consumption rate of ZrCl is equivalent to the mole production rate of ZrCl is introduced. It means that if electrode potential is more negative than the potential for the restriction criterion, produced ZrCl from Zr^{4+} is reduced into Zr completely.

Results

Eight reaction rate constants for Zr metal formation reaction from ZrCl were utilized and chemical form of cathode deposits for each case were estimated by the computational model as represented in TABLE II. For all reaction rate constants, calculated chemical form of the cathode deposits at 0.1 and 0.5 wt% $ZrCl_4$ salts were Zr metal without ZrCl. These results are identical to the lab-scale Zriclaoy-4 electrorefining experiments. At 1.0 and 2.0 wt% $ZrCl_4$ salts, chemical forms of zirconium compounds were dependent on the rate constant for the reaction producing Zr metal from ZrCl. As the rate constant increases, simulated weight fraction of Zr metal in the cathode deposits increases. When the rate constant was 1.0×10^{-3} and 1.5×10^{-3} m/s, computational modeling results agree with the results of the lab-scale electrorefining experiments: chemical form of the cathode deposits at the $ZrCl_4$ concentration of 1.0 wt% is a mixture of Zr and ZrCl and that of 2.0 wt% is ZrCl without Zr metal. This would mean that the reduction of ZrCl into Zr metal is much faster than the reduction of Zr^{4+} into ZrCl. However, for more accurate evaluation of the kinetics, quantitative benchmarking is required.

TABLE II. Computational modeling results on weight percent of Zr metal in the cathode deposits

Rate constants (m/s)		Weight percent of Zr metal in the cathode deposits [%]			
ZrCl/Zr	Zr^{4+}/ZrCl	0.1 wt% $ZrCl_4$	0.5 wt% $ZrCl_4$	1 wt% $ZrCl_4$	2 wt% $ZrCl_4$
1.0×10^{-6}		100	100	0	0
1.0×10^{-5}		100	100	0	0
1.0×10^{-4}		100	100	0	0
1.0×10^{-3}	1.69×10^{-4}	100	100	45	0
1.5×10^{-3}		100	100	51	0
2.0×10^{-3}		100	100	57	10
1.0×10^{-2}		100	100	90	62
1.0×10^{-1}		100	100	100	72
Experimental results		100	100	>0	0

PRELIMINARY SIMULATION OF ELECTROREFINING

The computational model with the equivalent Zr^{4+} reduction mechanism was utilized to simulate deposition of zirconium and uranium in a large scale electrorefiner. It was identified in the lab-scale electrorefining experiments that dissolution of Sn, Fe and Cr could be prevented by managing the anode potential, but uranium in the used nuclear fuel cladding could be dissolved into the molten salts during irradiated cladding electrorefining because uranium is more oxidative than zirconium. Therefore, reduction of uranium on the cathode was considered in the computational modeling with the multi-step reduction of Zr^{4+}. The rate constant of 1.5×10^{-3} m/s was used for the reaction between ZrCl and Zr. One-step reduction of U^{3+} into U was introduced in the computational model as follows:

$$U^{3+}+3e^-\rightarrow U.$$
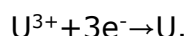
Mass production rate of ZrCl, Zr and U according to applied current was calculated.

Electrorefiner configuration

The electrorefiner containing LiCl-KCl-0.5 wt% $ZrCl_4$ with the height of 35 cm and the diameter of 80 cm was introduced for the computational modeling as Fig. 3. The rotating cylindrical cathode located at the center of the electrorefiner has the height of 25 cm and diameter of 15 cm and the rotating speed was assumed as 50 and 75 rpm. Three fan-shaped anodes with the height of 25 cm are fixed at the electrorefiner wall. It was assumed that irradiated Zircaloy-4 of 10 kg is loaded into the anode basket and there are uranium of 0.01132 wt% in the irradiated cladding [5]. In addition, it was assumed that all of the uranium in the cladding is

immediately dissolved into the molten salts. With these assumptions, the concentration of uranium in the molten salts was determined as 0.005 wt%.
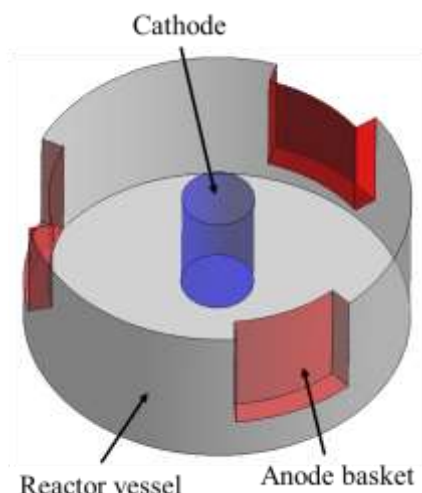

Fig. 3. Configuration of the electrorefiner used for the computational modeling on uranium and zirocnium deposition

Results and discussion

Local mass production rate distributions of ZrCl, Zr metal and U metal on the cathode were calculated. The distribution was almost equivalent in the circumferential direction but the distribution varied seriously in the vertical direction. Because of the edge effect of electric fields near the cathode, current was concentrated near the bottom of the cathode. For this reason, ZrCl started to be reduced to Zr metal and U was deposited from the bottom of the cathode. Therefore, ZrCl deposits were likely to be found near the top of the cathode but U metal deposits are likely to be observed near the bottom of the cathode.

Total mass production rate of ZrCl, Zr and U integrated over the cathode are represented in Fig. 4. Three current ranges were defined according to the types of the cathode deposits. When the applied current was not large enough as represented as the yellow region in the figures, ZrCl was not completely reduced into Zr. On the contrary, uranium is codeposited with Zr when high current is applied as represented as the red region. At the cathode rotating speed of 50 rpm, Zr can be recovered without ZrCl and U deposition in the applied current range between 11 and 32 A. The current range for Zr deposition is between 17 and 42 A. Since the limiting current density is inversely proportionate to diffusion boundary layer thickness, the current range where Zr metal without ZrCl and U can be obtained moved to a higher region when the rotating speed of the cathode was faster.
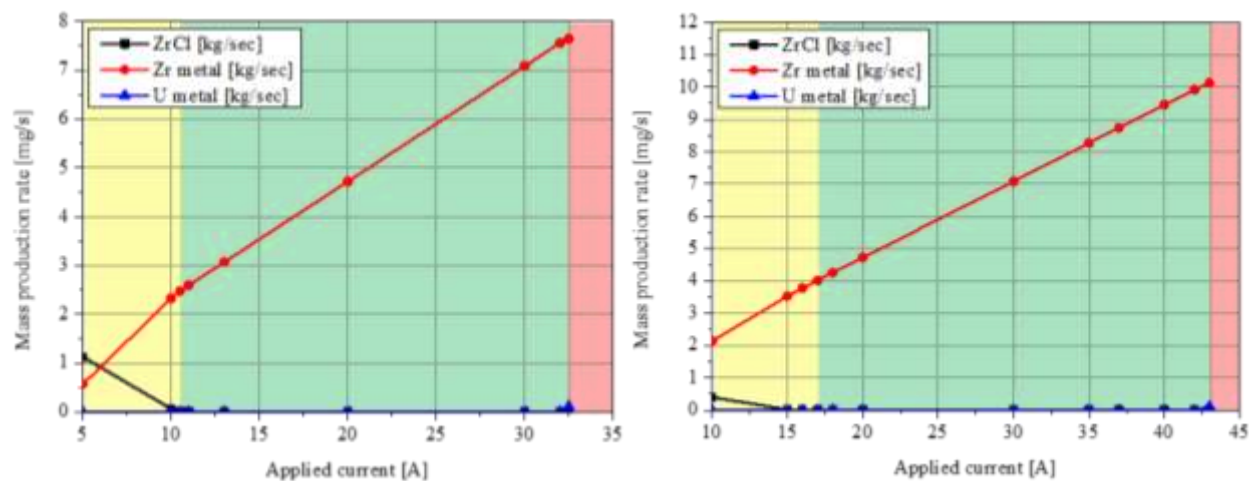
Fig. 4. Mass production rate of ZrCl, Zr and U according to applied current: rotating speed of the cathode is (left) 50 rpm and (right) 75 rpm

CONCLUSIONS AND FUTURE WORK

Lab-scale electrorefining of unirradiated Zircaloy-4 specimen in LiCl-KCl was performed, and high purity zirconium metal was obtained without ZrCl and other element deposition at 0.1 and 0.5 wt% $ZrCl_4$. Since the zirconium metal deposits were very powdery and detached from the cathode, further investigation to make coarse deposits or collect powdery deposits is needed. The computational model for electrorefining was utilized to simulate electrorefining experiments and it was identified that the computational model could handle the multi-step reduction of Zr^{4+} on the cathode. Reductions of zirconium and uranium ions were simulated with the computational model in the geometry of a preliminary designed electrorefiner for irradiated Zircaloy claddings. Operating conditions that can lead to the formation of zirconium metal without ZrCl and uranium were drawn. However, because benchmark of the electrorefining experiments was conducted qualitatively, further quantitative and sophisticated benchmarks are needed to utilize the computational model for designing an electrorefiner.

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