

Electrodeposition Behavior of U into Liquid Cd Cathode at Low Current Density

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1. Introduction

Pyroprocessing at KAERI is composed of electroreduction, electrorefining and electrowinning processes. Among them, the electrowinning is an electrochemical process to recover actinides using a liquid cadmium cathode (LCC). According to the U-Cd phase diagram [1], U and UCd_{11} are, respectively, present as a stable phase above and below $473^{\circ}C$ when both U and Cd elements coexist at such temperatures. U metals deposited on the surface of the LCC around $500^{\circ}C$ tends to form a dendrite shape having a large surface area and the U dendrites floating on the surface of the LCC have a role of a solid cathode, and from that time, co-deposition of U and TRU can be hampered[2,3]. If the UCd_{11} phase does not have a dendrite form during electrodeposition, this phase may sink into the liquid Cd. This can be a good method to simplify the equipment configuration through the omission of the stirring tool. In this study, the deposition behavior of U metal was observed when electrodeposition using a LCC was carried out at 450 and $500^{\circ}C$ at low current density.

2. Methods and Results

2.1 Experimental procedures

$LiCl-KCl-4wt\%UCl_3$ for these experiments was made by the chemical reaction of U metal and $CdCl_2$. An alumina vessel having an inner diameter of 15cm and an inner depth of 15cm was used as an electrolytic container. This salt has a hygroscopic tendency and thus the atmosphere needs to be maintained at very low oxygen and moisture. The glove box maintained an atmosphere of below 10 ppm oxygen and 1 ppm moisture content throughout all of the experiments. Three kinds of electrodes, reference, cathode, and anode, were used for this study. A pyrex tube containing $LiCl-KCl-1wt\%AgCl$ and silver (Ag) wire having a diameter of 1mm was used as a reference electrode. Both solid tungsten (W) and LCC were used as a cathode. W cathode was utilized to check the performance of the reference electrode because the pyrex reference tube is frequently broken, especially at the start time of the experiments. Liquid Cd of 210 to 400g as the cathode material was contained in alumina crucibles for the deposition experiments, where the crucibles having an inner diameter of 5cm and inner depths of 4.5cm were

utilized. W wire having a diameter of 1mm was used as Cd lead to pass currents into the liquid Cd, where the wire was shrouded by an alumina tube for the insulation. U metal or glassy carbon rod was employed as an anode. A salt stirrer was normally rotated at 70 to 100 rpm for the stirring of the salt. Chronopotentiogram was obtained at 450 and $500^{\circ}C$ at a current density of 50 mA/cm^2 .

2.2 Deposition behavior

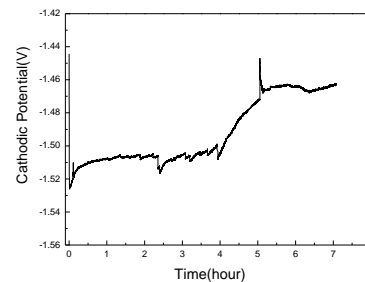


Fig. 1 Chronopotentiogram of U at the current density of 50 mA/cm^2 at $500^{\circ}C$



Fig. 2 U dendrite growth out of the LCC alumina crucible after the 7-hour deposition

Fig. 1 shows the variations of the cathode potential at the current density of 50 mA/cm^2 at $500^{\circ}C$ in $LiCl-KCl-4wt\%UCl_3$ salt. Cd of about 400g contained in an LCC alumina crucible was melted at $500^{\circ}C$ and then used as a cathode, where the diameter and inner depth of the alumina crucible were 5cm and 4.5cm, respectively. The concentrations of U ions in the salt will be constant throughout the deposition because U metal was used as an anode for this experiment. After the deposition proceeded for 2 hours, the alumina crucible was lifted above the electrolytic container and visually examined to check whether U dendrite grew out of the LCC alumina crucible or not. U deposit was not

observed until that time, and thus the alumina crucible containing liquid Cd was immersed back into the salt. U ions in the salt were continuously deposited on the LCC at the same current density. The cathode potential began to go upward right after the 4-hour deposition and arrived at the peak at about 5 hours, and from then on, little change occurred in the cathode potential, as shown in Fig. 1. The alumina crucible was again lifted upward to check the deposition status. Silver-colored U dendrite grew out of the alumina crucible, and both some liquid Cd with silver color and some of the salt above the Cd overflowed into the left bottom of the alumina crucible, as shown in Fig. 2. It was predicted that the liquid Cd and salt flowed out of the crucible along the needle-shape U dendrite.

Another U deposition experiment was conducted using cadmium of 210g and an alumina crucible having an inner depth of 4.5cm. In this case, only a third of the inner depth of the crucible would be filled with the liquid Cd. Fig. 3 shows the variation of the cathode potential at 50mA/cm² and 450°C. The cathode potential increased from -1.8V to around -1.7V during the initial deposition, remained nearly constant at -1.7V for 30 minutes, dropped to about -1.8V, and finally went upward again above -1.7V. Because the potential behavior is related to the electrode area, this potential behavior is considered to show that some deposits were created on the liquid Cd and then sunk into the Cd, and finally, another deposit was formed on the Cd. To visually check the deposition status, the alumina crucible was lifted above the electrolytic container. Even though there was a large potential variation during the deposition in this experiment, U deposits were not observed outside the alumina crucible, as shown in left of Fig. 4. The salt above the Cd contained in the LCC alumina crucible was removed with a spoon to check the deposit shape on the Cd. A deposit was protruded from the liquid Cd as shown in right of Fig. 4.

A few things can be explained from the above deposition experiment conducted at 450°C. According to the U-Cd phase diagram [1], a UCd₁₁ phase can be created below 473°C when liquid Cd is used as the cathode for the deposition of U. When the UCd₁₁ phase is created by the chemical reaction of the U and Cd during the deposition, a large potential change can occur due to the abrupt volume change of the material because an intermetallic compound such as UCd₁₁ can be made by an exothermic reaction. The sudden volume change of the liquid cathode leads to the variation of cathode potential. It was predicted from the above experiment that even though the density of the UCd₁₁ phase was not known yet in the literature, the created UCd₁₁ phase can be settled down into the Cd. Several authors published that an intermetallic compound such as PuCd₆ sunk into the Cd [4]. If UCd₁₁ sinks into the liquid Cd, a clean Cd surface can be maintained throughout the deposition without a Cd-stirring device, and it will be very helpful to simplify the design of the electrowinning equipment.

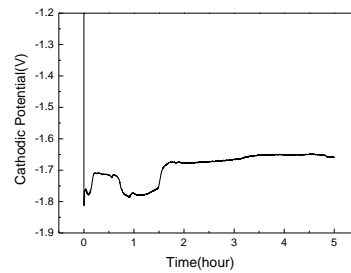


Fig. 3 Chronopotentiogram of U at the current density of 50 mA/cm² at 450°C



Fig. 4 Before (left) and after (right) the elimination of the salt in the LCC alumina crucible

3. Conclusions

To observe the deposition behavior of U when using a liquid cadmium cathode (LCC), several deposition experiments were conducted in the LiCl-KCl-UCl₃ salt at a current density of 50 mA/cm² at 450 and 500°C. At 500°C, the U metal deposited on the LCC grew in the form of a dendrite shape having a large surface area, and thus it was not sunk into the liquid Cd even though the density of U was much larger than that of liquid Cd. On the other hand, the UCd₁₁ phase was stable according to the U-Cd phase diagram at 450°C. It was observed from this study that the UCd₁₁ phase did not have a dendrite shape and could be sunk into the liquid Cd during the electrodeposition without a Cd-stirring device.

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