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Electrodeposition of Uranium on Cadmium Cathode Depending on the Deposition Temperature

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1. Introduction

Electrowinning is a electrochemical process to simultaneously recover transuranium as well as uranium by using a liquid cadmium cathode (LCC). U ions are known to be deposited on the LCC in the form of dendrites having large surface area. These U dendrites were difficult to settle down into the liquid Cd even if the density of U was even larger than that of Cd [1]. The floating U dendrites on the LCC have a role of solid cathode and so co-deposition of U and TRU could be hampered. So, LCC agitators have been developed to prevent U from forming dendrites, for example, blade stirrer and pounder in Japan and United States, respectively [1, 2].

According to the U-Cd phase diagram [3] of Fig. 1, U or UCd_{11} phases are, respectively, stable above and below 473°C when both U and Cd elements are coexisted. Up to now, electrodeposition experiments of actinides on the LCC have usually been carried out above 473°C, especially at around 500°C [1-3]. If UCd_{11} phases do not have a dendrite form in the process of a electrodeposition, these phases may sink into the liquid Cd even when no-stirring of LCC. This will be a good method to enhance the recovery rates of actinide elements. In this study, we observed if the UCd_{11} phases could go down to Cd without a stirring of LCC.

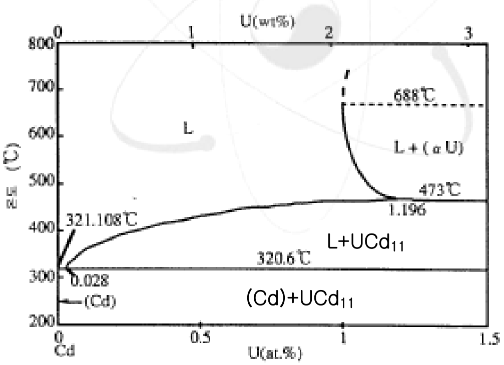


Fig. 1 Uranium-Cadmium phase diagram

2. Experimental Procedures

Fig. 2 shows an electrowining apparatus used in this study. About 0.25 kg of LiCl-KCl-2wt%UCl_3 salt and about 0.32 kg of Cd metal were contained in an alumina vessel (150 mm ID) and an alumina cathode crucible (50 mm ID), respectively. A Mo wire having a diameter of 1 mm was used as a lead of LCC. This lead wire was inserted into a protective alumina tube having 1.5 mm in inner diameter and 3 mm in outer diameter. About 5 mm of Mo was exposed out of the protective tube and then sealed to prevent the molten salt or the liquid Cd from flowing into the protective tube. And also, an alumina tube (scraper) having 4 mm in inner diameter and 6 mm in outer diameter would scrape the U deposits attached to the protective tube. This scraper tube moved along the protective tube every 20 minutes.

A SUS basket containing uranium metal chips and a pyrex tube having LiCl-KCl-1wt%AgCl salt were used as an anode and a reference electrode, respectively. During the electrodeposition process, an alumina salt stirrer was continuously rotated at 40 rpm in the salt vessel to help U ions to migrate into the LCC. But, cathode stirrers were not used in this study. The electrodeposition experiments were conducted at 430°C and 500°C at a current density of 100 mA/cm^2. All the experiments were carried out in a glove box under an Ar atmosphere below 10 ppm of water and oxygen.

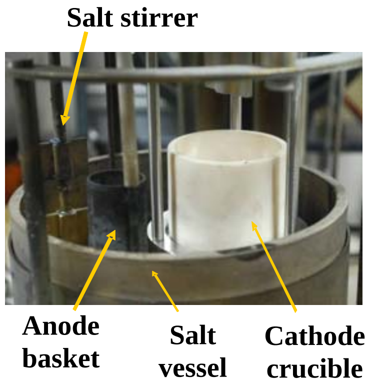
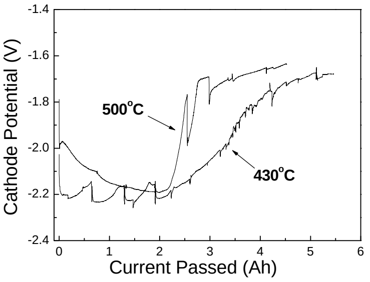


Fig. 2. Electrowinning apparatus used in this study.

3. Results and Discussion

Fig. 3(a) shows the change of the cathode potentials depending on the deposition temperature. At a temperature of 430°C, the cathode potential was relatively stable until 2 Ah (ampere hour) even if 3 peaks were created. These peaks were formed due to the movement of the srcaper tube into the LCC. The potential began to decrease after 2 Ah and got to about -1.7 V around 5 Ah. At 500°C, the cathode potential gradually increased until 2 Ah and then began to sharply decrease to around -1.65V around 4 Ah.



(a) Cathode potential

(b) 430°C (c) 500°C

Fig. 3. U electrodeposition results at the temperatures of 430°C and 500°C.

The solubility of U elements was known to be roughly 2.3wt% in liquid Cd at 500°C [3]. The potential of the LCC gradually increased when the actinides were dissolved into the liquid Cd [4]. And, a rapid decrease of the cathode potential after the solubility limits was related to the increase of the cathode area [5].

Our results could be explained by using the above literature materials. Some of the U elements deposited at 500°C were probably dissolved into the liquid Cd in the early deposition stage because the cathode potential showed the gradual increase until 2 Ah as shown in Fig. 3(a). And, the cathode area would begin to increase after 2 Ah because the cathode potential rapidly started to decrease since then.

U elements deposited on the liquid Cd below 473°C were considered to form UCd_{11} precipitates according to the U-Cd phase diagram of Fig. 1. Solid precipitates such as $PuCd_6$ did not influence the potential of LCC [4]. From these data, the 430°C result in Fig. 3(a) could be understood. That is, UCd_{11} precipitates were presumably formed from the early deposition stage and most of the precipitates did not sink into the liquid Cd. And, U elements would be continuously deposited on the floated UCd_{11} phases and then grow out of the cathode crucible.

After the deposition experiments were terminated, the cathode crucibles were taken out of the salt vessel to check the deposition status. U deposits have different forms, that is, granules and dendrites at 430°C and 500°C, respectively. As above-mentioned, each deposit grew out of the cathode crucibles within 5 Ah as shown in Fig. 3(b) and Fig. 3(c). It is, therefore, considered that LCC agitators should be developed to efficiently oppress the dendrite formation.

4. Conclusions

Some information was obtained from the deposition experiments depending on the temperature. When the deposition experiment was conducted at 500°C, U elements were dissolved into the liquid Cd in the early deposition stage and deposited in the form of dendrite beyond the solubility limit of U in Cd. These U dendrites having a large surface area would be floated on the Cd surface and so became grew out of the cathode crucible. The U elements deposited at 430°C were considered to form UCd_{11} precipitates from the early deposition stage. These solid precipitates did not sink into the liquid Cd and these U deposits were also grew out of the cathode crucible. Thus, it is considered that LCC agitators should be developed to efficiently oppress the dendrite formation.

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