

Uranium Deposition on the Liquid Cadmium Electrode Depending on the Stirring Methods

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1. Introduction

Liquid cadmium cathode (LCC) in a pyrochemical process [1] has been used as an electrode to co-deposit transuranium (TRU) and uranium (U). By the way, U elements have a tendency to form dendrites during the electro-deposition. These dendrites have a large surface area and do not sink into the liquid cadmium (Cd). In that case, the U dendrites floated on the surface of Cd have a function of solid cathode and the co-deposition of TRU and U could be hindered. In order to oppress the formation of these U dendrites, a pounder stirrer and a paddle stirrer have been developed in United States and Japan, respectively [2,3]. The paddle stirrer could be operated only by a rotary motor but the pounder requires two operation modes such as a rotation and a vertical movement. In the present work, the function of a paddle stirrer was evaluated depending on the stirring methods.

2. Methods and Results

About 2.5 kg of LiCl-KCl-2wt%UCl₃ 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. A STS basket containing U metal chips and a pyrex tube having LiCl-KCl-1wt%AgCl salt were used as an anode and a reference electrode, respectively.

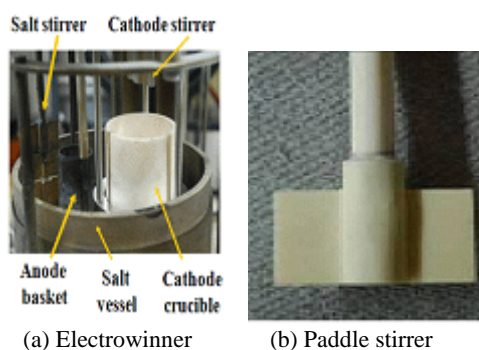


Fig. 1 Electrowinning apparatus.

Fig. 1 shows an electrowinner and an alumina paddle stirrer used in this study. During the electrodeposition process, a paddle stirrer was continuously rotated at 40 rpm in the salt vessel to help U ions to migrate into the LCC. Another paddle stirrer for the stirring of LCC was laid to the interface of Cd and salt or into the Cd.

Hereafter, each stirring method will be named an interface stirring and a deep stirring, respectively. The

electrodeposition experiments were conducted at 500°C at current densities of 50, 100 and 200 mA/cm². All the experiments were carried out in a glove box under an Ar atmosphere below 10 ppm of water and oxygen.

2.1 Deep Stirring

Fig. 2(a) shows the change of the cathode potential at a current density of 100 mA/cm² in the deep stirring. The initial cathode potential was around -1.8 V and the potential gradually decreased as the deposition time increased. This means that the reduced U was not dissolved into the Cd [2]. When the passed current approached to -3.8 Ah (ampere hour), the deposition stopped to identify the status of U deposition on the cathode crucible. No U deposits were observed on the edge of the crucible. The 2nd deposition experiment was serially conducted for about 2 Ah. Even if the initial cathode potential of the 2nd experiment was not the same with the final potential of the 1st deposition experiment, the cathode potential of the 2nd deposition reached the extended value which is approximately predicted by the slope of the cathode potential of 1st experiment.

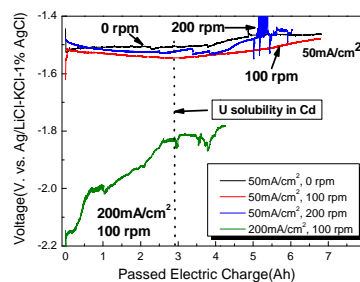
Fig. 2(b) shows the appearance of the paddle stirrer and the cathode crucible after the 2nd experiment. U deposits were not seen on the top edge of the cathode crucible but some deposits attached to the rod of the paddle stirrer were exposed to the salt surface contained in the cathode crucible. When the stirrer was lifted upwards, a large volume of U deposits attached to the rod of the paddle stirrer were seen. On the other hand, only a small volume of deposits were attached on the inner wall of the cathode crucible. Most of the U was thought to be preferably deposited on the rod even if the rod was made of ceramic material. This is not a desirable deposition process and therefore a tool to prevent U to be deposited on the rod should be used to enhance the efficiency of the deep stirring method.

2.2 Interface Stirring

Fig. 3(a) shows the change of the cathode potentials depending on the current densities and the revolution speeds in the interface stirring. Completely different potential profiles were obtained at 50 mA/cm² and 200 mA/cm². Even at 50 mA/cm² the potential profile showed different trends whether the stirrer was used or not. In the case of no-stirring at 50 mA/cm², the cathode

potential began to decrease from the beginning meaning that the reduced U was not soluble to the liquid Cd and began to form dendrite on the surface of Cd. In the case of stirring, the cathode potential increased from the beginning to 3 Ah and then continuously decreased. It reflects that the stirrer helped the reduced U to be dissolved to the liquid Cd up to 3 Ah which corresponds to the U solubility limit in Cd and the reduced U began to grow in the form of U dendrites after 3 Ah. If the revolution speed is excessively fast, for example, 200 rpm, not only U dendrites but also liquid Cd could overflow out of the cathode crucible because of the high centrifugal force. Therefore, the proper revolution speeds should be decided to stop the overflow of U deposits.

At 200 mA/cm² the potential began to decrease very rapidly from the beginning even if the stirrer was operated. This is probably because the reduction rates from UCl₃ to U were greater than the dissolving rate of U to the liquid Cd at 200 mA/cm² and so U dendrites began to form on the Cd surface nearly from the deposition beginning. U dendrites were predicted to grow out of the cathode crucible within 3 Ah at 200 mA/cm². It is judged from the above results that the stirrer did not prevent the dendrite growth at high current densities.



(a) Cathode potential

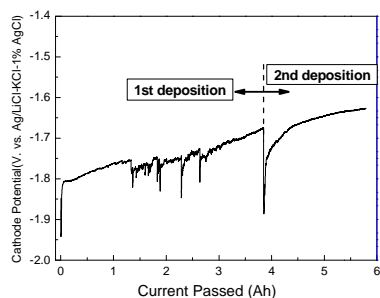


(b) 50 mA/cm², 200 rpm (c) 200 mA/cm², 100 rpm

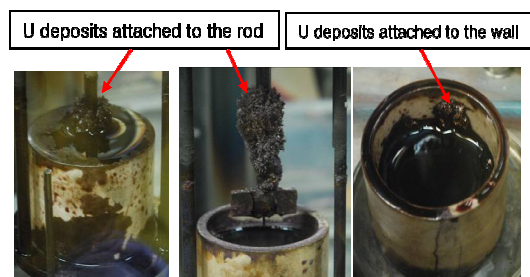
Fig. 3 Cathode potential and uranium deposition status on the cathode crucibles depending on the current densities and the revolution speeds in the interface stirring.

3. Conclusions

Some experiments were conducted to compare the stirring methods by a paddle stirrer. In the deep stirring a lot of U elements were deposited to the rod of the paddle stirrer to show that this method could not nearly put U deposits into the liquid Cd. The interface stirring helped U elements to be dissolved into the liquid Cd only up to the U solubility limit. Anyway, the paddle stirrer could oppress the growth of U dendrites out of the cathode crucible just up to 4Ah irrespective of the stirring methods. More efficient tools were required to oppress the growth of U dendrites.



(a) Cathode potential



(b) U deposits on the cathode crucible

Fig. 2 Cathode potential and uranium deposition status on the cathode crucible at 100 mA/cm² in the deep stirring

Acknowledgements

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