

Characteristics of graphite cathode for uranium electrorefining

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1. Introduction

There are great progresses in pyrometallurgical reprocessing areas of spent nuclear fuels, since the last decade [1~3]. In this process, an electrorefining in molten chlorides is the main step and the efficiency of the process is one of the requirements for the treatment of a large volume of uranium in an integrated area, so many attempts have been made to enhance the throughput of the electrorefiner [3,4]. The main concepts to enhance the throughput are to increase the cathode area and decrease the physical distance between the electrodes as well as to continuously operate the electrodeposition process without any interruptions. To realize these, Mark-IV and Mark-V electrorefiners were developed and as a result the Planar Electrode Electrorefiner (PEER) was developed by the Argonne National Laboratory (ANL) [5]. The PEER was designed to obtain a higher throughput by enhancing the electrode area and independent operation for the scraping of the uranium deposit. However, such electrorefiners using a steel cathode have insurmountable characteristics in terms of a sticking during a scraping of the deposit. To remove the remaining adhered deposit, a stripping operation in which the polarity is reversed to clean up the cathode surface should be periodically performed. This stripping operation has been known to be one of the main factors that decreases the current efficiency [3]. Hence, in this study, we would like to report on a new electrorefiner concept by introducing a graphite cathode to minimize the sticking of the uranium deposit.

2. Experimental

The electrorefining apparatus was installed in a glove box filled with high-purity Ar gas as shown in Fig. 1 and the detailed experimental conditions can be found elsewhere [6]. Only difference is that the steel cathode was replaced with a graphite cathode. The graphite cathode is not rotated during an electrodeposition and the molten salt itself is agitated by means of a crucial anode basket containing metallic uranium. The scrapped uranium deposit was collected by a deposit collector located beneath the cathode. High purity LiCl-KCl eutectic(41.5-58.2 mol%, T_m :355 °C) as an electrolyte was purchased from the Johnson Matthey Company. The chloride of the trivalent uranium was extracted by an oxidation reaction between the depleted uranium metal in the anode basket and $CdCl_2$ and the



Fig. 1. Glove box for the uranium electrorefining.

concentration was set at (to) 9 wt% of LiCl-KCl. Electrodeposition tests were performed at 500 °C by the use of an Ecochemie Autolab 30 potentiostat controlled by a computer system. The graphite cathodes were weighed before and after an experiment to calculate the sticking coefficient (S.C.) as follows;

$$S.C. = \frac{\text{quantity of U retained on cathode surface(g)}}{\text{theoretical deposition quantity of U(g)}} \quad (1)$$

3. Results and discussion

It was observed that the uranium was deposited on to the graphite cathode at 30 mA/cm² of the applied current density as shown in Fig. 2, with a sticking coefficient of 0.62. However, this value is below that (about 0.8) of a steel cathode after a scraping [3]. Also, as the current density increased to 100 mA/cm², the

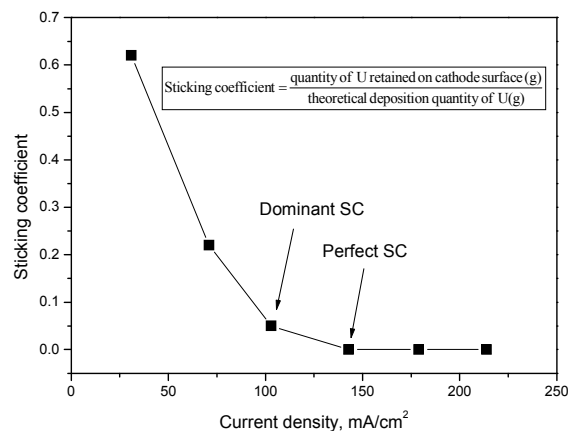


Fig. 2. Variation of sticking coefficient of graphite cathode according to current density (500 °C, UCl_3 : 9wt%, SC : self scraping).

sticking coefficient drastically decreased to 0.06 and finally no uranium deposit was observed on the graphite cathode, which means a self-scraping behavior. It is very surprising that the uranium deposit fell so spontaneously during an electrorefining at such a high current density, because the scraping of the U deposit has been a challenge to and one of the determinant steps for the efficiency of the electrorefining process. In order to explain the self-scraping phenomena of the graphite cathode, the formation mechanism of the U-graphite intercalation compound (U-GIC) was introduced in author's former research [7]. This mechanism starts from the fact that the radius of the uranium atom (3.5 Å)

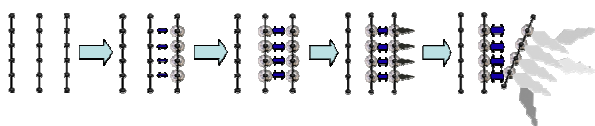


Fig. 3. Schematics of the self-scraping mechanism of graphite cathode during electrorefining of uranium

is larger than the initial inter-plane distance of the graphite (3.354 Å). Hence, there should be an elongation like Fig. 3 in the graphite planes as the uranium forms GIC [8]. When the gravitational force of uranium dendrite deposited exceeds the bonding strength of the elongated graphite's utmost layer, a self-scraping occurs by itself. Here, a contamination of carbon should not be a problem because uranium dendrites grow successively on the pre-formed dendrites, thus the measured carbon content was only about 300 ppm. Furthermore, such an amount of carbon in uranium can be physically removed by an yttrium reaction during the casting step of a uranium deposit [9]. The self-scraping mechanism of the graphite cathode was also confirmed by the fact that the cathode potentials were measured to be more positive at above 100 mA/cm² when compared to that of the steel cathode. Fray et. al. reported that the more positive discharge potential of



electrorefining of uranium (500 °C, UCl₃ : 9wt%, current density : 130mA/cm² for 3 hrs).

lithium at a graphite electrode than that at a molybdenum electrode attributed to the occurrence of a lithium intercalation into the graphite[10]. After an electrorefining of the uranium graphite cathode it exhibited a clean surface as shown in Fig. 4 and the uranium deposit was successfully recovered by a collector.

4. Conclusion

Electrorefining experiments were successfully carried out in LiCl-KCl eutectic molten salt with a graphite cathode. It was found that the formation of U-GIC helped the self-scraping mechanism of the uranium dendrite and that it should increase the efficiency of the electrorefiner due to an elimination of the stripping step. These are only qualitative preliminary experimental results but we believe that further research on this type of activity change the direction of the electrorefining research on spent nuclear fuel.

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