The Effect of Processing Parameters on the Deposition Behavior of a Spent Fuel Surrogate in the Molten Salt Electrorefining

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Abstract

The electrorefining experiments with an anode composed of U, Y, Gd, Nd and Ce (or U, Gd, Dy and Ce) were carried out in the KCl-LiCl eutectic melt at 500 °C. Uranium was the major component in the cathode deposits at the high initial uranium concentration, and the separation factors of the uranium with respect to the rare earths (REs) were calculated according to the applied voltage and the uranium concentration in the molten salt. The current efficiency was inversely in proportion to the applied voltage in the range of 1.0 V to 1.9 V (vs. STS304L). The dependency of the applied voltage on the current efficiency as well as the deposition rate was discussed in terms of the microstructural feature and crystal structure of the deposit.

Key Words : electrorefining, eletrodeposition, molten salt, separation factor, dendrite

1. Introduction

During last decade, interests in the pyrometallrugical treatment of spent nuclear fuel have been drastically increased because of its relatively low processing cost as well as its proliferation resistance of the nuclear fuel cycles[1,2]. More recently it has become one of the important requirements to recover long-lived nuclides, since the geological disposal of high level waste is encountering big difficulties in obtaining public acceptance. Also, the recovered Uranium, transuranium(TRU) and rare earth elements (REs) can be utilized as a fuel source again and as functional materials. From this point of view, the recovering of long-lived nuclides is awakening new interests in the fuel cycle process not only for reprocessing but also for the partitioning and transmutation of transuranium elements. Among the proposed pyrometallrugical reprocesses, only a couple of methods based on electrochemical separations have been investigated intensively and developed to a plant

scale. The Argonne National Laboratory(ANL) and the Russian Institute for Atomic Reactors(RIAR) are pioneering groups who have developed the pyrometallrugical reprocessing routes. The main streams of these routes are divided into the electrorefining process of irradiated alloy fuel from the Integral Fast Reactor(IFR) concept and the electrochemical reduction of oxides from the chlorinated irradiated oxide fuel both in a molten salt.

The main scientific and technological interests in the electrochemical process are how to effectively partition a spent fuel into Uranium, TRU and fission products(FPs). For this, vast researches have been conducted as a matter of national policy. However, there are still a few fundamental obstacles to be overcome such as understanding the interaction among the species in a molten salt, microstructural change of the deposits according to the processing parameters and its effect on the total yield. Furthermore the systematic investigation of the electrorefining characteristics of the uranium in a chloride coupled with crystal structural evaluation have not been reported[3~9]. Hence in this study, a series of electrorefining processes was performed on a spent fuel surrogate to obtain the optimum processing parameters for enhancing the partitioning efficiency of the components.

2. Experimental

The electrorefining apparatus is shown in Fig. 1 schematically. The solid cathode with a rugged groove can be rotated during electrodeposition to achieve a better recovery and the molten salt itself is also agitated by means of a submerged stirrer. An alumina catch dish was located underneath the cathode to collect any deposits dropping off. A deposition rate was calculated by weighing the deposit scraped from the cathode after washing and dividing it by the bare cathode surface area and deposition time. The anode, cathode and reference electrode were STS 304L for the chloride molten system. High purity LiCl–KCl eutectic(41.5–58.2 mol%, T_m:355 °C) as a chloride electrolytes and rare earth salts of 99.9% purity were purchased from Sigma–Aldrich. All the chemicals were handled in the glove box in which both the oxygen and water contents in the argon atmosphere were maintained lower than 10 ppm. The alumina cell was located in a stainless steel thermowell which was heated externally with an electric furnace attached to the floor of a glove box.

The temperature was controlled at 500 °C and the melts were stirred at the rate of 75 rpm throughout the experiment. Electrodepositions were performed by the use of an Ecohemie Autolab. 30 potentiostat controlled by a data acquisition system. First preliminary solid cathode tests were carried out by using LiCl–KCl eutectic salt containing uranium, yttrium and three REs(Gd, Nd and Ce). The concentrations of the total metal ion were kept at 3~10 wt% throughout the experiment. The yttrium and three REs which have similar electrochemical characteristics with TRU were formulated as a spent fuel surrogate, since

there are difficulties in handling of the TRU in Korea. Especially, a series of electrorefining with the REs(Gd, Dy, Ce) was performed separately, in order to more precisely confirm the feasibility to use Ce and Dy as TRU surrogates. The concentration of the uranium and REs in the molten salt and deposits were determined by ICP-AES. The crystal structure was analyzed by X-ray diffractometer with CuKα. The morphologies of the micro deposits were analyzed by a compact micro vision system(HIROX KH-2200MD2) after removing the attached salt from them.
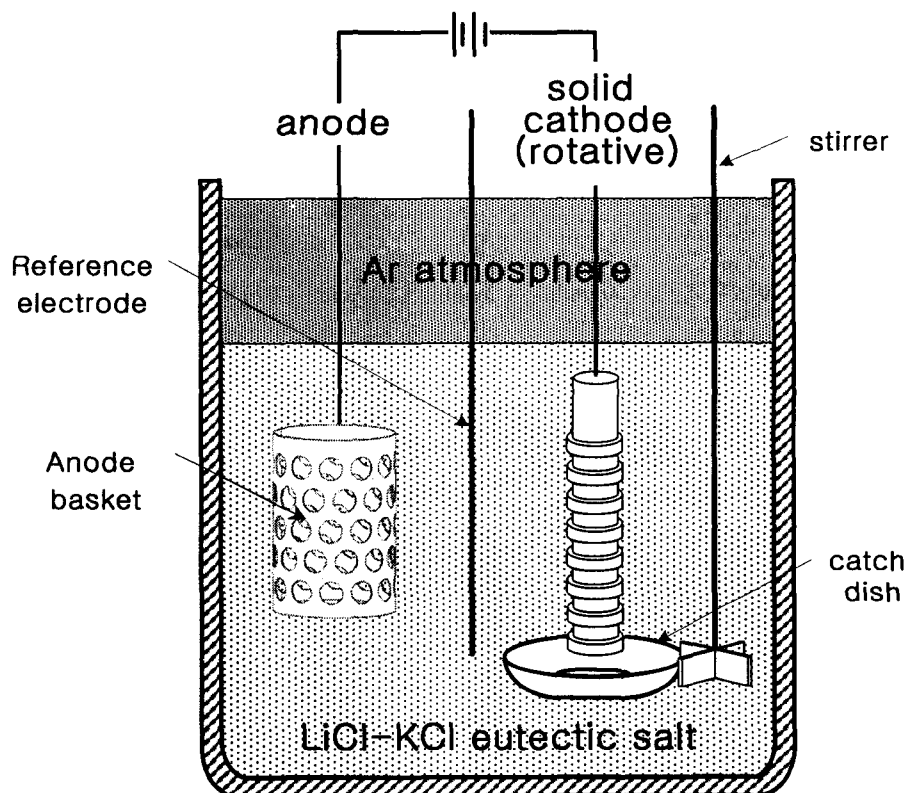

Fig. 1. Experimental apparatus for molten salt electrorefining

3. Results and discussion

Typical cyclic voltammogram of the chloride molten salt system is shown in Fig. 2. Four peaks occur during the complete potential sweep cycle; two cathodics corresponding to the electrochemical reduction of the UCl_3 and REs choride at -1.4 and $-1.9V$ respectively, and two anodics corresponding to the dissolution of the uranium and REs as the potential sweep is reversed. Figure 3 shows the effect of an applied voltage on the current efficiency and deposition rate of the chloride molten salt systems containing uranium and REs. The current efficiency was calculated as follows;

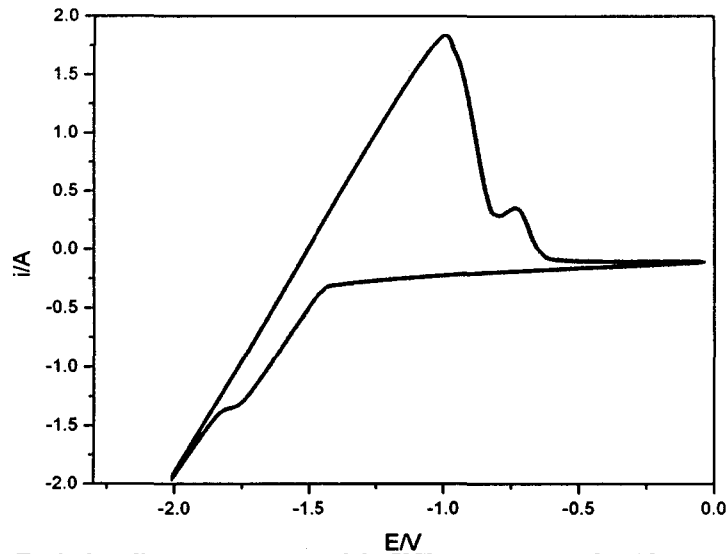$$Current\ Efficiency(\%) = \frac{Y_a}{Y_t} \times 100 \tag{1}$$

Fig. 2. Typical cyclic voltammogram of the UCl₃ and REs in KCl-LiCl eutectic at 500 °C
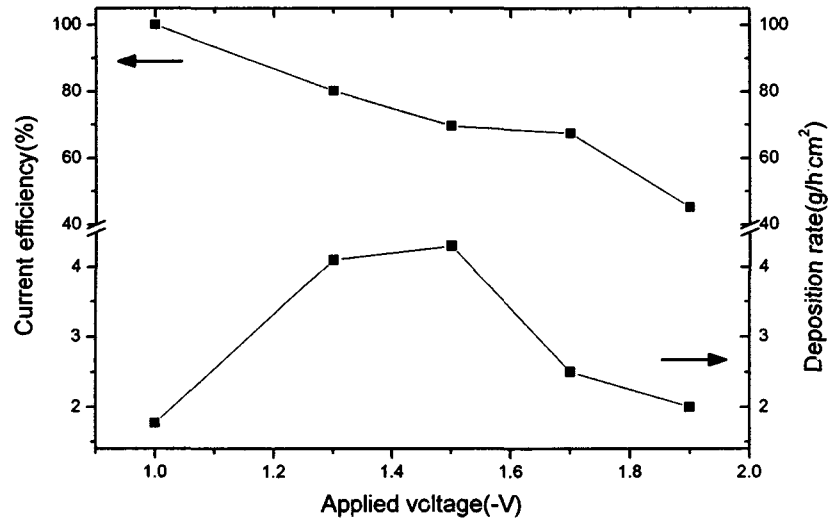(scan rate: 100mv/s).

Fig. 3. Effect of the applied voltage on the current efficiency and deposition rate
(initial U concentration in molten salt: 3wt%).

Where Y_a and Y_t are the actual yield and theoretical yield of the deposits that would have been collected based on the electrodeposition current (ampere–hours), respectively. The current efficiency was calculated as 80~100 % whereas it decreased as the applied voltage increased. The size of the deposit decreases as the applied voltage increases because the nucleation sites by the discharged metal ions increase on the cathode surface. Other possible reasons for the potential dependant morphology are the kinetic selection and twinning processes [11], however further explanations are not accessible for the present

experiments. Hence, the lower yields of the deposits at a higher applied voltage are because the deposit particle size decreased as the applied voltage increased and then some of the deposits occasionally fell not only from the cathode but also out of the catch dish in the case of the finer particles. Generally a large quantity of eutectic salt adheres to the cathode deposits which could also decrease the metal fraction in the total deposit. The deposition rate increased as the applied voltage increased up to $-1.5V$, and then decreased after that. It is believed that $-1.0V$ was too low for the uranium halogenides to decompose and deposit on the cathode, and the decreasing of the deposition rate at above $-1.5V$ may connect with the morphological characteristic of the deposit as aforementioned.

The overall current efficiency according to the measured cathode current density is depicted in Fig. 4. It is clearly seen that the current efficiency decreases as the cathode current density increases. Based on the ohm' s low, a current density increases in proportion to an applied voltage. Hence the decrease of the current efficiency can be interpreted by the decrease of the deposit particle size.
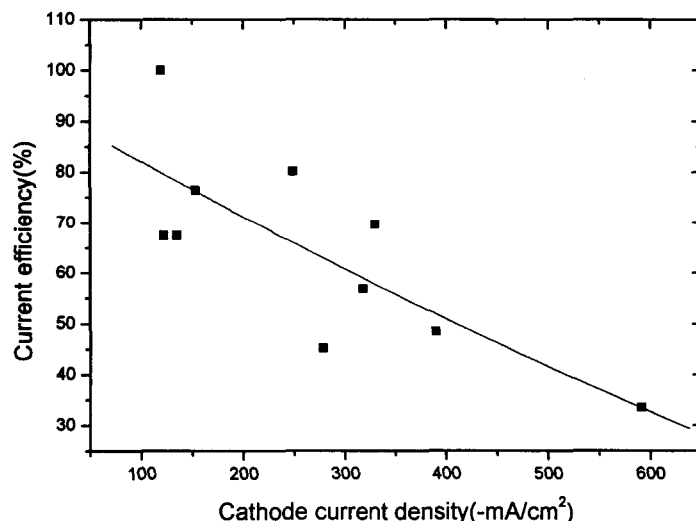
Fig. 4. Effect of the current density on the current efficiency

(initial U concentration in molten salt: 3wt%).

In order to closely check the effect of the current density on the morphology of the deposit, microphotographs of the deposit on the cathode were taken after removing the adhered salt as shown in Fig. 5. The deposits formed by electrorefining are generally observed as a dendrite structure. The morphology of the deposit drastically changes according to the current density as well as the initial uranium concentration in the molten salt. A whisker like dendrite structure was found at a relatively low uranium concentration
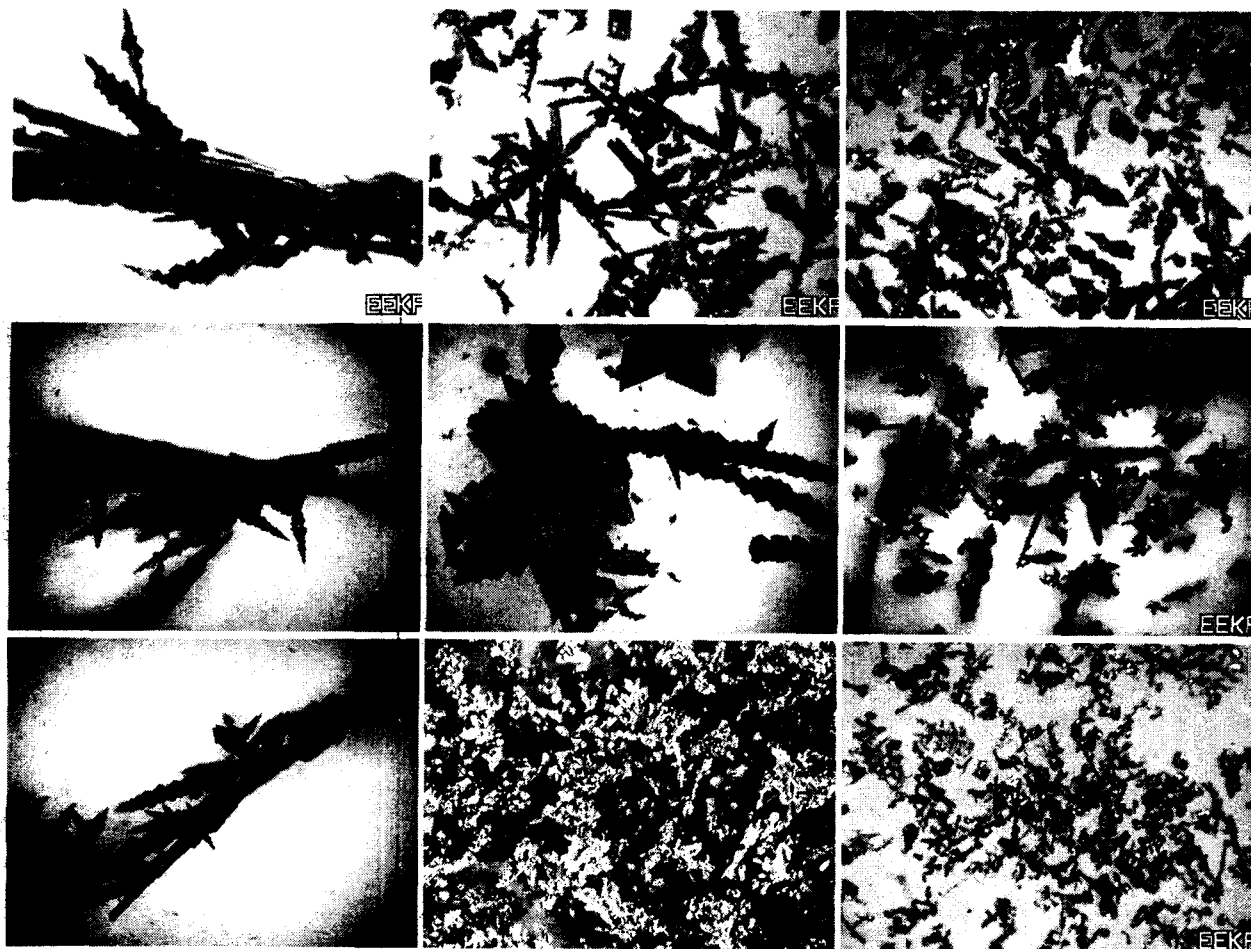
Fig. 5. The microstructure of the deposited uranium according to the current density at different initial uranium concentrations (electrorefining time:1800sec).

a) -97 mA/cm^2	b) -174 mA/cm^2	c) -310mA/cm^2	at 3wt% of U
d) -87 mA/cm^2	e) -156 mA/cm^2	f) -326mA/cm^2	at 6wt% of U
g) -35 mA/cm^2	h) -109 mA/cm^2	i) -373mA/cm^2	at 9wt% of U

(3 wt%) and a low applied current density (50 mA/cm^2), see Fig. 5 a), d) and g). In this case, the deposition rate is low. It should be noted that the current density also changes the needle like dendrite shape into a rhombic crystal. When the current density is relatively low below 100 mA/cm^2, the formation of a whisker like dendrite is dominant, whereas the rhombic dendrite structure is formed predominantly at a higher current density above 300 mA/cm^2. In the middle of the current density, whisker like and rhombic dendrite were formed simultaneously as shown in Fig. 5 b), e) and h). In order to clarify the crystal structural change with the current density, X-ray diffraction patterns were obtained on the uranium deposit as shown in Fig. 6. It was confirmed that the deposit on the cathode is α-uranium(JCPDS No. 24-0748) with (021) and (002) equally developed. The (021) plane was drastically decreased, practically invisible, as the applied current increased and any other peaks are also eliminated. It is believed that that the growth of (002) plane should be

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relatively easy in terms of the accumulation of electric charge, hence leads the formation of plate like rhombic uranium crystal structure. However the determinant step of the deposit morphology is not clear with this data, so the morphological change of the deposit with electrorefining time was investigated as shown in Fig. 7. In the initial period (900 sec) of the formation of the deposit, Fig. 7 a), fine dendrite pieces are formed on the surface of the cathode. Succeeding the dendritic growth a metallic crystal starts to form from the sharp edge of the deposit on which an applied current is concentrated, Fig. 7 b). As the deposition time increased to 1800 sec, rhombic or whisker like dendrite grow, Fig. 7 c), and a further increase of the deposition time promoted the formation of the rhombic dendrite chain, Fig. 7 d).
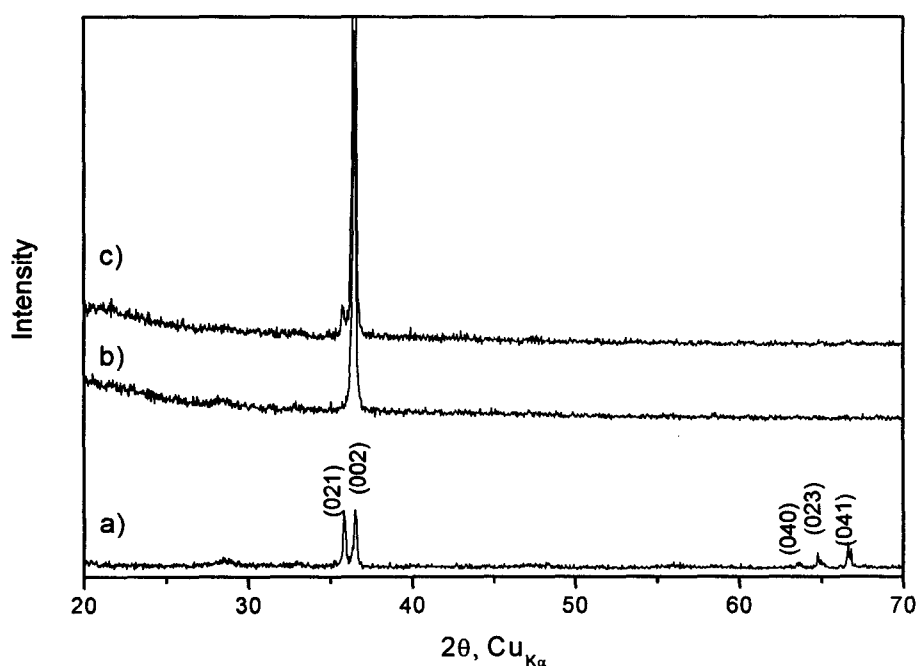

Fig. 6. X-ray diffraction patterns of uranium obtained from different current density.

a) 40mA/cm^2 b) 100mA/cm^2 c)200mA/cm^2

A series of electrorefining with the REs(Gd, Dy, Ce) according to an initial U concentration in the molten salt to precisely confirm the feasibility to use Ce and Dy as TRU surrogates. In the relatively high initial U concentration of 5.6 wt%, nearly pure U was deposited on the cathode surface in the whole range of applied voltage and Gd, Dy and Ce were hardly observed in the deposit as shown in Fig. 8. However, REs concentration on the cathode surface increased especially at relatively high applied voltage, as the initial U concentration decreased. It was observed that the fraction of U in the deposit in the range of 1.5~2.0 wt% up to −1.5V was generally observed high, however sharply decreased as the applied voltage increased. The REs content in the deposit at above −1.7 V in the 1.5 wt% of UCl$_3$ exceed the U content. Furthermore, all the REs except Gd were main deposit in
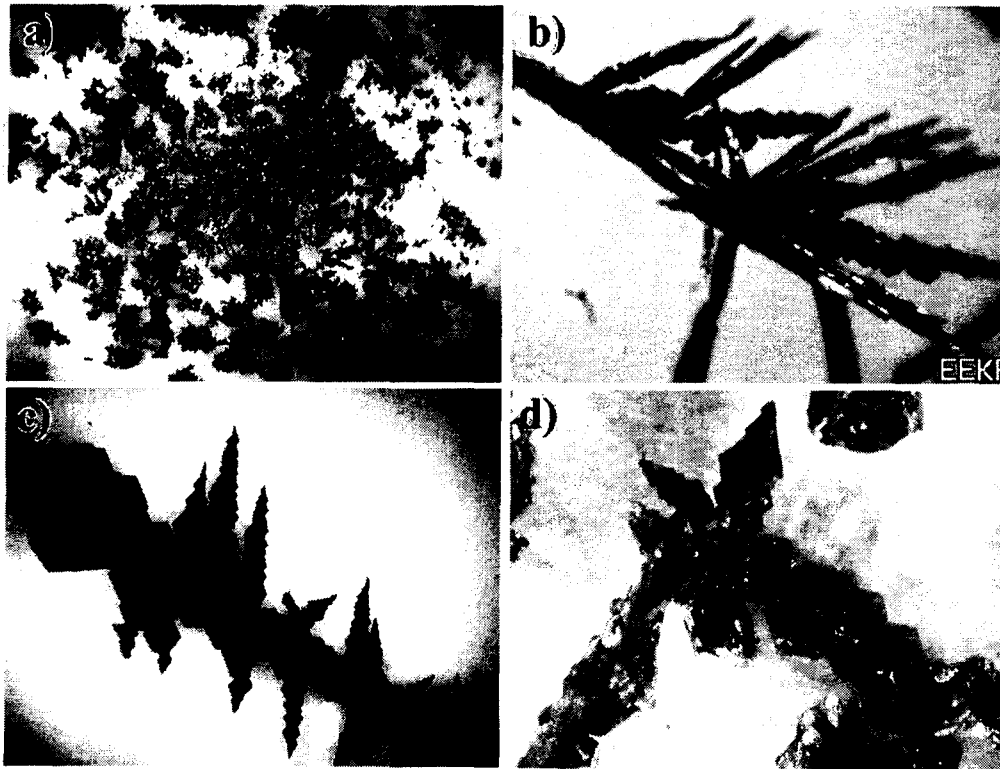
Fig. 7. Dendrite development pattern according to the electrorefining time

(initial U concentration in molten salt: 3wt%, current density:-242mA/cm^2).

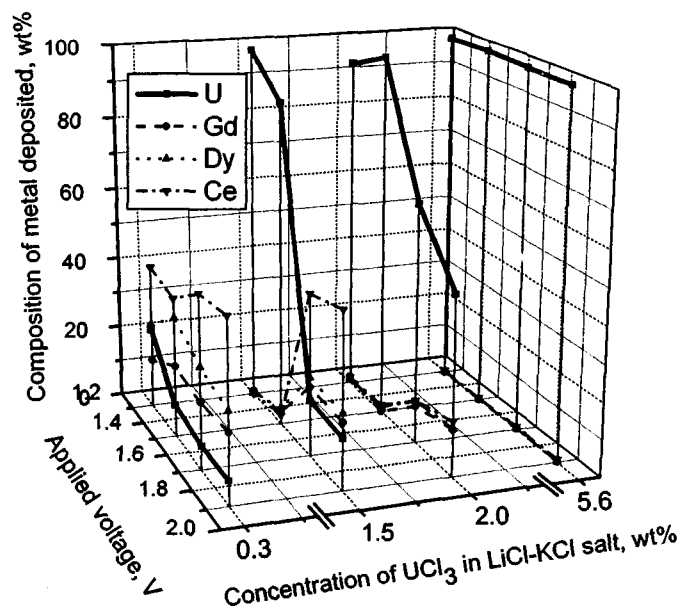a) 900 sec   b) 1200 sec   c) 1800 sec   d) 3600 sec

Fig. 8. Dependences of applied voltage and initial UCl$_3$ concentration in LiCl-KCl

salt on the composition of metal deposited at 500 °C.

the whole range of the applied voltage at 0.3 wt% of initial UCl_3 concentration. Also, it should be noted that the deposition rate of Dy and Ce are found to be higher than U at this concentration of UCl_3 regardless of the applied voltage. This is because trivalent REs such as Dy and Ce deposits are oxidized in the presence of sufficient uranium chloride as follows;

$$M_{(cathode)} + NCl_{3(salt)} \rightarrow MCl_{3(salt)} + N_{(cathode)} \qquad (2)$$
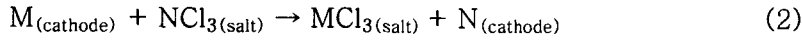
where M and N are REs as a TRU surrogate and U respectively.

From these phenomena, it could be interpreted that Dy and Ce exhibit the similar characteristic with REs at the high U concentration, while they behave like TRU chloride as U concentration decreases.

The partitioning characteristic between two elements is estimated by introducing separation factor defined by Sakamura et al.[13,14] as follows;

$$SF_M = \frac{(X_{M\,in\,Salt})/(X_{M\,in\,Deposit})}{(X_{N\,in\,Salt})/(X_{N\,in\,Deposit})} = \frac{D_M}{D_N} \qquad (3)$$

Where $X_{M,N\,in\,Deposit}$ and $X_{M,N\,in\,salt}$ are the mole fractions of M or N in a cathode deposit and in salt, D is the distribution coefficient. Separation factor of the U vs. REs as a function of an initial U concentration at 1.5V of applied voltage is shown in Fig. 9. It is clearly seen that the separation factors of REs to U below 2 wt% of initial U concentration are not high and nearly same each other, whereas they increased as the U concentration increased above 2 wt%. Hence the U concentration in the LiCl−KCl eutectic molten salt should be kept more than 2 wt% to effectively separate pure metallic U on the cathode surface.
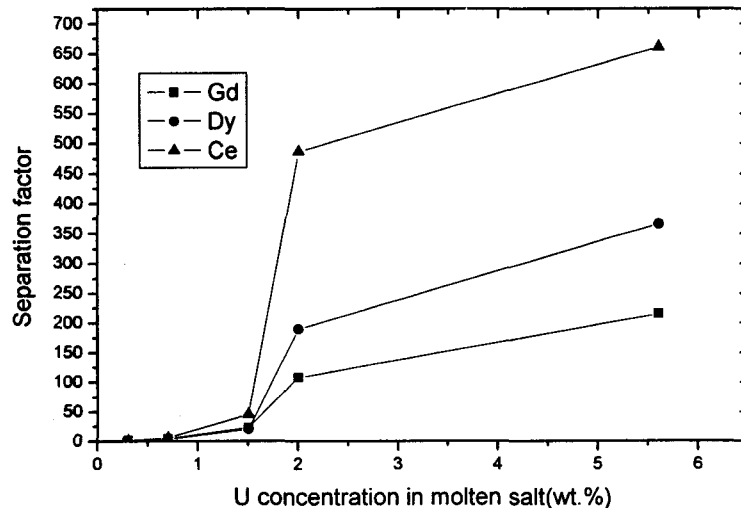

Fig. 9. Separation factor on U concentration in salt (applied voltage : -1.5V)

Electrorefining experiments were carried out in LiCl−KCl eutectic molten salt containing uranium and RE chlorides. The cathode current efficiencies rapidly decreased as the applied voltage increased, and the highest separation factor was achieved at −1.5V which is little higher value than the reduction voltage of the uranium chloride. The efficiency decreases according to the applied voltage were attributed to the morphological features of the deposits. The fraction of REs in the deposit sharply increased as the applied voltage reached the reduction voltage of the RE chlorides, −1.9V. When the initial U concentration in molten salt was more than 2 wt%, Ce and Dy exhibited REs behavior while the deposition behavior started to change to that of TRU as the concentration decreased under the 2 wt%, which means they are codeposited with U on the cathode surface. Hence Ce and Dy could be applied as TRU surrogate materials and the U concentration in molten salt electrorefining process should be kept more than 2 wt% in order to clearly separate U from spent fuel.

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