

Electrochemical Formation of Bi-Hf Alloy in LiCl-KCl for Actinides Separation Process by Density Distribution

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1. Introduction

The pyrochemical processing technology for recycling spent nuclear fuel has been developed to recover useful resources and to reduce the longevity of final wastes with the enhanced proliferation-resistance and accident-tolerance. Liquid metal cathodes are effectively used in the pyroprocessing [1, 2]. It is desirable for the proliferation resistance that solubility of actinides in liquid metal are low enough to co-electrodeposit TRU elements as intermetallic particles. It is reported that liquid bismuth is better than liquid cadmium in terms of the greater lanthanide to actinide separation factor [3]. Also the density of Bi is located between lanthanides and actinides, therefore, separation performance can be enhanced. In this study, we investigated electrochemical behavior for Hf element on liquid Bi cathode and potentiostatic electrolysis was carried out. Hf was chosen as an actinides surrogate since Hf has similar redox potential on Bi cathode and intermetallic density with Bi compared with actinides.

2. Experimental

2.1 Apparatus and materials

Experiments were carried out in a glove box filled

of argon gas with 99.999% purity. The oxygen and moisture concentrations were maintained below 0.1 ppm. The temperature of molten salts was maintained at 500°C to a stability within $\pm 2^\circ\text{C}$. Three electrodes system was applied to electrochemical experiments. Liquid Bi and graphite rod were utilized for working electrode and counter electrode, respectively. Reference electrode was Ag/AgCl (1wt. %). Eutectic LiCl-KCl (Sigma Aldrich, 99.99%) and HfCl₄ (Alfa Aesar, 99.9%) was used as an electrolyte.

2.2 Experiments

CV technique was employed to investigate the redox behavior on the liquid Bi film electrode and to identify electrochemical intermetallics formation of Bi and Hf. To produce Bi film electrode, BiCl₃ was loaded into the molten salt at 500°C. When the potential scan is started from Bi reduction potential toward to negatively, Bi³⁺ is reduced to the tungsten and then Hf can be reduced to the Bi filmed electrode. Potentiostatic electrolysis was carried out to form Bi-Hf alloy. After electrolysis, liquid Bi cell was solidified to reveal the vertical distributions. The ingot cross section was microscopically and crystallographically analyzed to investigate the stoichiometry of intermetallic phase and the vertical location of intermetallic particles in Bi.

3. Results and Discussions

3.1 Cyclic voltammetry

Figure 1 presents cyclic voltammogram of HfCl₄ (1.20wt.%) on liquid Bi electrode at 500°C. As the scan was made from positive to negative potential, Bi³⁺ is reduced to Bi metal and the Bi metal is filmed at the W electrode surface at around +0.2 V. The second reduction peak and the second oxidation peak are attributed to redox couple of Hf⁴⁺ on the Bi film electrode. As the redox peak seems to be irreversible, exchange current density was explored prior to derive apparent standard potential. Tafel plot was built and exchange current density is calculated to be 3.13E-2 A/cm². Apparent standard potential is derived to be -1.047 V.

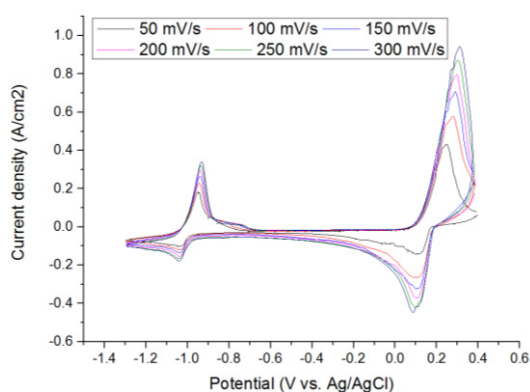


Fig. 1. Cyclic voltammogram of LiCl-KCl-HfCl₄ (1.20wt.%) on liquid Bi film working electrode at 500°C.

3.2 Potentiostatic electrolysis

Potentiostatic electrolysis were carried out to produce Bi-Hf alloy at 500°C. Constant cathodic potential of -1.1 V was applied that the potential was determined from the apparent standard potential derived by CV. The top phase is equivalent to the liquid Bi cathode surface. Almost all intermetallics was shown to locate at the bottom of Bi. The

boundary layer seems to be clarified between Bi bulk and Bi-Hf intermetallic riched phase. Hf was not found from the stoichiometric analysis by EDS for the Bi bulk. Regarding the detection limit of on the EDS apparatus is within the range of 1 at. %, Hf can be attributed to exist as much as its solubility in Bi. For the bottom phase, the atomic ratio of Hf to Bi is close to 1 for the intermetallics particles by EDS and that can be explained to HfBi. Since the density of liquid Bi and HfBi is 9.75 g/cm³ and 12.6 g/cm³, respectively, the results of spatial distribution of HfBi is reasonable. Also, Hf is shown to be separated in liquid Bi media.

4. Conclusions

In order to investigate actinides behavior in liquid Bi electrode, Hf was selected as a surrogate and CV and electrolysis was carried out. Electrochemical redox behavior was observed from the CV. As the results of electrolysis, HfBi intermetallics were analyzed at the bottom of the Bi alloy and it is well agreed with the density information. Therefore, the feasibility of actinides separation could be shown in Bi.

REFERENCES

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