Distribution of Zirconium Between Salt And Bismuth During A Separation From Rare Earth Elements By A Reductive Extraction

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SUMMARY

It was studied on the reductive extraction between the eutectic salt and Bi metal phases. The solutes were zirconium and the rare earth elements, where zirconium was used as the surrogate for the transuranic(TRU) elements. All the experiments were performed in a glove box filled with argon gas. Two types of experimental conditions were used –high and low initial solute concentrations in salt. Li-Bi alloy was used as a reducing agent to reduce the high chemical activity of Li. The reductive extraction characteristics were examined using ICP, XRD and EPMA analysis. Zirconium was successfully separated from the rare earth elements by the reductive extraction method. The LiF-NaF-KF system was favorable among the fluoride salt systems, whereas the LiCl-KCl system was favorable among the chloride salt systems. When the solute concentrations were high, intermetallic compounds were found near the salt-metal interface.

INTRODUCTION

The pyrometallurgical process is useful to separate long-lived radionuclides from the spent fuel. The obtained long-lived radionuclides can be artificially transmuted to short-lived

or stable nuclides by the technology so-called "nuclear transmutation". Therefore, the technologies are very prospective to consider the disposal and reuse of the spent fuel [1,2].

The high-level radioactive waste contains various kinds of metals and metal oxides such as actinide, rare earth, noble metal, alkaline, and alkaline earth elements. Among the various elements, TRU elements are recovered with a small amount of rare earth elements and uranium in the electrorefining process. The reductive extraction process is an important step to refine the recovered TRU product from the electrorefining process for the preparation of the transmutation reactor fuel.

In this study, it was investigated on the distribution of zirconium between salt and bismuth during a separation from rare earth elements by a reductive extraction.

EXPERIMENTAL

All the experiments were performed in a glove box filled with argon gas (Fig.1). The Li-Bi alloy was used as a reducing agent to reduce the high chemical activity of Li. The solutes were zirconium and some rare earth elements, where zirconium was used as the surrogate for the transuranic(TRU) elements.

The pyro-coated graphite crucible loaded with the eutectic salt, solutes, and Bi metal was placed at the bottom of the furnace. And then, the salt and metal phases were agitated with a two-blade tantalum impeller at a rate of 60 rpm after five hours of heating at 100°C above the meting point of the salt. Two types of experimental conditions were used –high and low initial solute concentrations in salt. The Li-Bi alloy was added at an interval of about 5 hours.

The salt phase was sampled with an alumina rod by dipping. A metal Bi sample was drawn with an alumina tube and a syringe. The above sampling procedures were repeated

after each addition of the Li-Bi alloy. After the extraction experiment, the frozen Bi metal was cut into several horizontal slices using a diamond saw to examine the concentration profile of the metal phase. The reductive extraction characteristics were examined using ICP, XRD and EPMA analysis.

RESULTS AND DISCUSSION

Due to the high reaction temperature, the reduction was relatively fast. The distribution equilibrium was attained in less than 3 hours after the reductant addition. The concentrations of the solute elements in the salt phase decreased and the concentrations in the Bi phase increased with the increasing time. Zirconium was reduced most easily, whereas europium was the most irreducible element among the solute elements. It was found that zirconium could be separated from the rare earth elements effectively.

There was no good material balance between the decreased amount of the solute in the salt phase and the increased amount in the Bi phase. This was probably due to the formation of the intermetallic compound or the formation of the oxy fluoride. EPMA analysis was carried out to confirm the formation of the intermetallic compounds between Bi and reduced metals. Figure 2-a shows the SEM image of a sliced sample of Bi metal that was prepared by sawing horizontally the frozen Bi phase. There are many gray spots and they are considered to be intermetallic compounds. The EPMA spectrum of the reduced metals is shown in Figure 2-b. The reduced metals were only found in a dark spot and the concentration of Zr, the most reducible element, was higher than the other metals.

LiF-NaF-KF and LiF-BeF_2 were used as the fluoride eutectic salt systems. LiCl-KCl and LiCl-NaCl were used as the chloride eutectic salt systems. The separation factors of two

fluoride salts were similar, but the toxicity of Be is so high that the $LiF-BeF_2$ system is hard to use as a process salt. In the LiCl-NaCl system, it was found that Na was extracted into Bi metal phase during reductive extraction experiments. Therefore, among the chloride salt, the LiCl-KCl system is more favorable than the LiCl-NaCl system from the point of view of separation factor and stability of the eutectic salt.

SUMMARY

The following conclusions were attained from the study.

- Equilibrium was attained within three hours after addition of Li reductant.

- The LiF-NaF-KF system was favorable among the fluoride salt systems, whereas the LiCl-KCl system was favorable among the chloride salt systems.

- At high initial solute concentrations, intermetallic compounds were formed.

REFERENCE

[1] H. J. Dewey, "The Accelerator Transmutation of Waste Concept Overview", Report LA-UR-93-2895, Los Alamos National Laboratory, USA (1993).

[2] L. M. Ferris, J. C. Mailen, J. J. Lawrence, F. J. Smith and E. D. Nogueira, Trans. Am. Nucl. Soc. **12**, (1969) 26

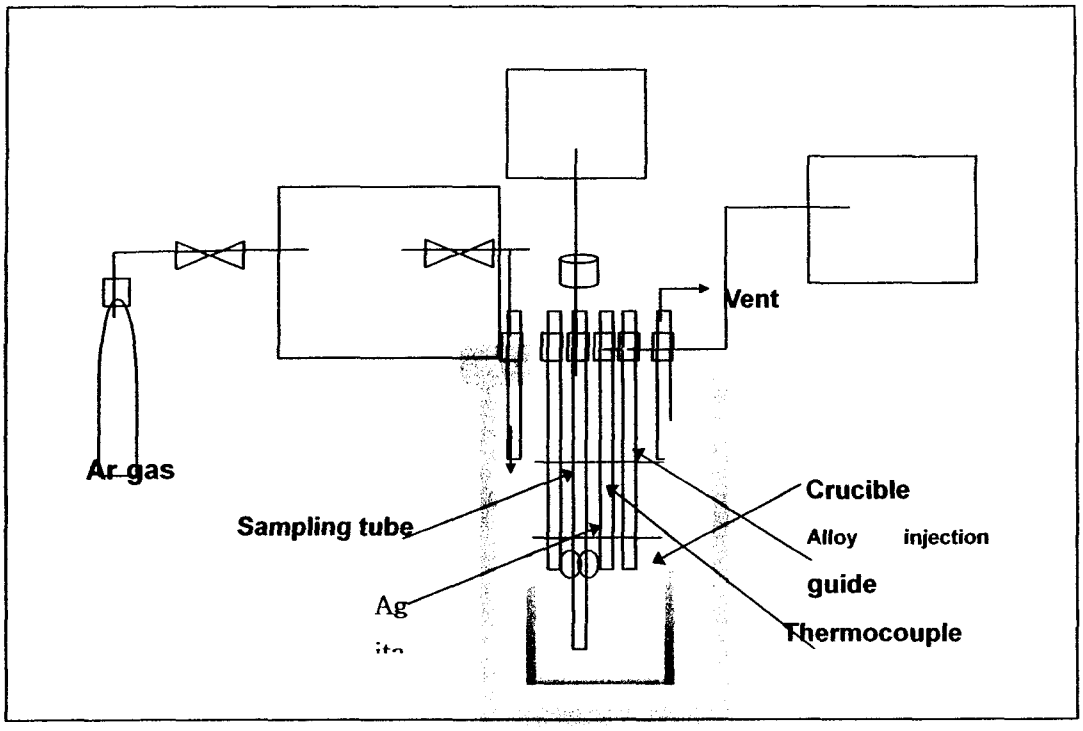
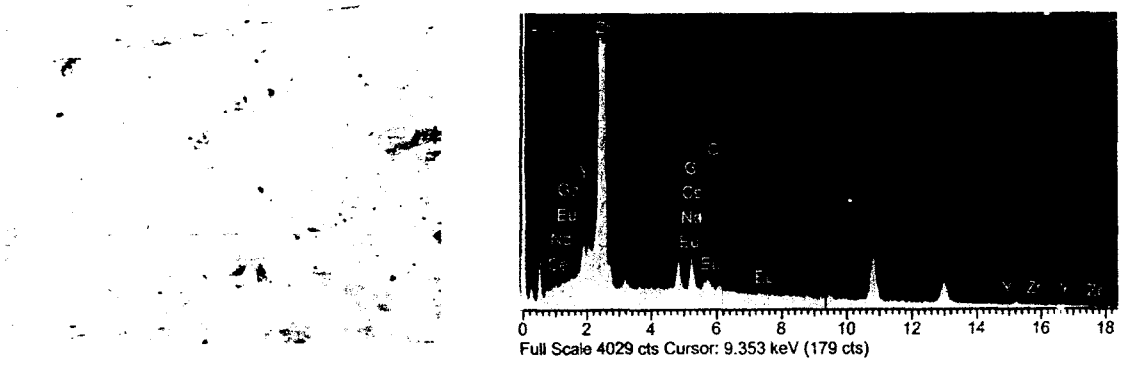


Fig. 1. Schematic diagram of the experimental set-up for the reductive experiments.



(a) (b)

Fig.2. Analysis of the Bi phase (a) SEM image of the layer at 10.5mm below the interface and (b) EPMA spectrum on gray spot in Bi phase after fre