Transactions of the Korean Nuclear Society Spring Meeting
Chuncheon, Korea, May 25-26 2006

Chemical Behavior of Lanthanide Oxides and Uranium(III) in a LiCl-KCl eutectic melt at 723 K

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1. Introduction

Recently, molten alkaline chloride based melts are considered as a promising reaction media for future nuclear programs and more specifically for spent fuel processing.(1-2) The use of this technology for pyrochemical processing of spent nuclear fuel is emerging as a promising option in the near future. However, rare earth elements (REEs) contained in spent fuel may pose a potential problem for related pyrochemical processes. Therefore, it is necessary to understand the chemical nature of the actinides and lanthanides in high-temperature melt. Here, we report some basic physicochemical properties of REE oxides and their reactivity with U(III) in a LiCl-KCl eutectic melt at 450 ° C.

2. Experimental

All the experiments were carried out in an Ar atmosphere glove box to avoid exposure to oxygen and water. The LiCl-KCl eutectic (41.5 mole% KCl) mixture (melting point 634 K) was prepared from LiCl (Aldrich) and KCl (Aldrich). Dried salts were mixed and melted under purified Ar atmosphere. The oxygen and H_2O level was maintained to be less than 2 ppm. Home-built UV-VIS spectrometer combined with optical fiber technology was used to measure the lanthanide behavior in LiCl-KCl melt at 723 K. A Bruker EMX spectrometer operating at X-band frequency was used for recording EPR spectra. An Edinburgh FS920 fluorometer with the excitation sources from a 450 W Xe-lamp and Hamamatsu R955 PMT was used for recording luminescence spectra.

3. Results

Solubility of lanthanide oxides:
We have studied the solubility of various lanthanide oxides in LiCl-KCl eutectic melt at 723 K. In general, lanthanide oxides appeared to be insoluble/sparingly soluble in LiCl-KCl eutectic at 723 K. However, europium oxide exhibited abnormal behavior in solubility and redox chemistry. The solubility of europium oxide was measured to be ~3 orders of magnitude higher than those of other lanthanide oxides. Figire 1.

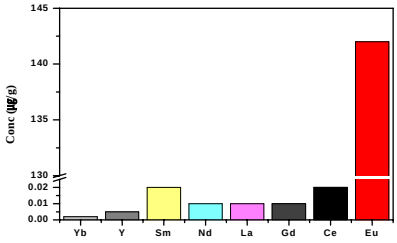

Figure 1. Solubility measurement of lanthanide oxide in LiCl-KCl melt at 723 K.

This abnormal solubility may be attributable to different electrochemical behavior of europium in the same experimental conditions. Most lanthanide ions exist as trivalent oxidation states. However, we identified the stable divalent europium dissolved in LiCl-KCl molten salt by applying electron paramagnetic resonance (EPR) and luminescence spectroscopic methods.

Reactivity of U(III) with lanthanide oxides:
UV-VIS spectroscopy provides essential information on the behavior of f-block elements in LiCl-KCl melt system.(3) We designed and built special apparatus and equipments for studying the behavior of uranium and lanthanides in LiCl-KCl eutectic melt under controlled chemical conditions. We applied fiber optics technology to monitor the electronic spectra of uranium(III) and lanthanide elements in-situ at high temperature ionic melt. We obtained electronic spectra of U(III), Nd(III) and other lanthanide elements. The reaction of U(III) with lanthanide oxides in LiCl-KCl eutectic melt was studied by on-line monitoring the electronic spectra. Figure 2 presents the electronic spectra of U(III) and Nd(III). This spectra were obtained by in-situ monitoring of the reaction of U(III) with Nd_2O_3.

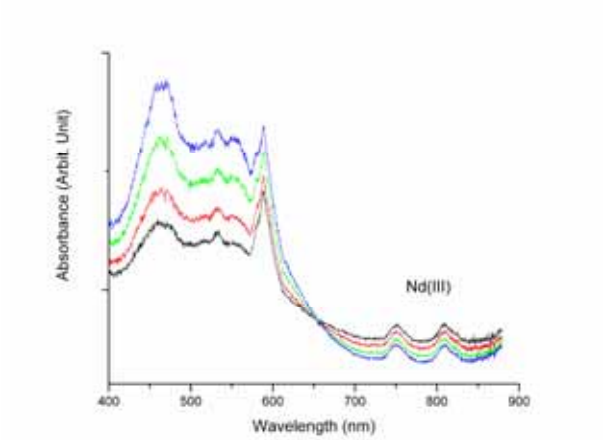

Figure 2. On-line monitoring of theUV-VIS spectra for the reaction of U(III) with Nd_2O_3 in molten salt.

It shows the changes in U(III) and Nd(III) simultaneously. The intensity of U(III) peak decreased as the reaction proceeded, and consequently the intensity of Nd(III) peak increased. In general, molar extinction coefficient of lanthanides are much lower than U(III). The reactions of U(III) with other lanthanide oxides (and Li mixed oxides) exhibited similar results.

By analyzing the UV-VIS spectra and XRD analysis of uranium precipitates, the reaction of U(III) with lanthanide oxides can be expresses as follows:

$2UCl_3 + Ln_2O_3 \rightarrow UO_2 + UO + 2LnCl_3$

Thermodynamic evaluation of the above reaction supported the experimental results.

4. Conclusions

Lanthanide oxides appeared to be insoluble/sparingly soluble in LiCl-KCl eutectic at 723 K. However, in the presence of U(III) all REE oxides dissolves by following reaction:

$2UCl_3 + Ln_2O_3 \rightarrow UO_2 + UO + 2LnCl_3$

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