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Thermodynamics and separation factor of uranium from lanthanum in liquid eutectic gallium-indium alloy/molten salt system

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ABSTRACT

This work presents the electrochemical study of lanthanum and uranium compounds in fused 3LiCl-2KCl eutectic *vs.* Cl^-/Cl_2 reference electrode in the temperature range 723–823 K on liquid gallium-indium eutectic alloy. Thermodynamics and the activity coefficients of lanthanum and uranium were studied. The separation factor of uranium from lanthanum on gallium-indium eutectic alloy was determined.

1. Introduction

Actinides recycling by separation and transmutation are considered worldwide as one of the most promising strategies for more efficient use of the nuclear fuel as well as for nuclear waste minimization, thus contributing to make nuclear energy sustainable. With this purpose, two major fuel reprocessing technologies have been explored for separation of the actinides from the fission products: PUREX (standard nuclear reprocessing method for recovery of uranium and plutonium from spent nuclear fuel (SNF) in aqueous solutions) and PYREX (nuclear reprocessing method for recovery of uranium and plutonium from spent nuclear fuel in molten salts).

At present non-aqueous pyrochemical methods employing molten salts and liquid metals are developed for reprocessing SNF of fast reactors. Inorganic melts have very high radiation stability and can be employed for organizing a short closed fuel cycle. Fissile elements and fission products dissolved in a salt melt can be separated employing selective extraction by liquid metals. Detailed information on the properties and behavior of all elements present in SNF in fused salts and liquid metals is required to design a feasible separation process and these include rare earth elements representing an important group of fission products. Selectivity of pyrochemical separation process taking place at the molten salt – liquid metal interface depends on the properties of both phases. Knowing thermodynamic properties of all SNF components in working media is essential for determining applicability of a particular system for practical application [1–25].

The electrochemical behavior of La^{3+} ions and thermodynamic properties of the reaction $La + {}^3/_2Cl_2 = LaCl_3$ in fused 3LiCl-2KCl eutectic were studied [26]. The equilibrium potential of La^{3+}/La couple was determined by using open circuit chronopotentiometry, with subsequent calculation of the apparent standard potential, and the apparent Gibbs free energy. The electrochemical behavior of UCl_3 in 3LiCl-2KCl eutectic melt was studied by different electrochemical methods [27]. The standard rate constants of charge transfer for electroreduction of uranium ($U^{3+} + 3\bar{e} \rightarrow U$) were calculated by the impedance spectroscopy method [27–29]. The thermodynamic stability of La(III) and U(III) complexes in 3LiCl-2KCl system was studied by electrochemical techniques [30]. There is single information about the separation factor (SF) of uranium from neodymium between the gallium-indium liquid alloy and 3LiCl-2KCl molten salt phases [31]. The separation factor of uranium from lanthanum in the same system is unknown.

The estimation of thermodynamic properties of liquid metals show that from all low melting metals gallium is most efficient in separating of lanthanides from actinides. The separation factor of U/La on liquid Ga is 14,000 and on liquid In – 190 at 1073 K, respectively [32]. Binary and ternary eutectic mixtures can be used to lower melting point of metallic alloys and thus the operation temperatures. Also some physical properties of liquid alloys are better than single components. Gallium-indium system offers one

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of the lowest melting eutectics with the melting point around 289 K and can be used multiply in industrial-scale production [33]. Vapor pressure of the metallic phase is another important factor to consider. Vapor pressure above the metallic eutectic alloys can be estimated from the additive rule and known temperature dependencies of vapor pressures of individual metals. For the Ga-In eutectic the vapor pressure is expected to be very low even at relatively high temperatures, *e.g.*, at 1100 K estimates give the value around $1.14 \cdot 10^{-7}$ atm. Thus the wide temperature range of the liquid state and low vapor pressures make Ga-In system very attractive for application in pyrochemical reprocessing of SNF. Lowering working temperatures simplifies technological process and construction of the apparatuses.

Behavior of lanthanum has so far been studied only in binary systems, La-Ga [34] and La-In [35] and the behavior of uranium – in binary systems, U-Ga [36] and U-In [37]. There is no information about the thermodynamic properties of lanthanum (uranium) and their separation factor in low melting metallic alloys.

In the present study the base thermodynamic properties of lanthanum (uranium) and the separation factor of uranium from lanthanum was determined on Ga-In eutectic alloy.

2. Experimental

The experiments were carried out in electrochemical quartz sealed cell with a three electrodes setup under dry argon atmosphere using potensiostat-galvanostat AUTOLAB PGSTAT 30 (Eco-Chimie) with specific GPES electrochemical software (version 4.9) at the temperature range 723–823 K.

For obtaining the dependence of the apparent standard redox potential $E^{*}{}_{La^{3+}/La}$ and $E^{*}{}_{U^{3+}/U}$ *vs.* the temperature the semi-galvanic cell (1) was used. The inert molybdenum electrode was polarized at potentiostatic conditions for a short time and after deposition a small amount of metal lanthanum (uranium) on the surface of working electrode the dependence of potential–time was measured. Lanthanum (III) ions were added in the solvent as $LaCl_3$ and uranium (III) ions - by electrolysis of the melt using metallic uranium anode. The concentration of lanthanum (III) ions in molten solvent was 1.0–2.0 wt. %. In this case the measurements were done by the potentiometry at zero current on inert working electrode as a molybdenum plate (Goodfellow, 99.9%) with a surface area of 0.5–0.6 cm^2. For obtaining the dependence of the apparent standard redox potential of alloy, $E^{**}{}_{La(Ga\text{-}In)}$ or $E^{**}{}_{U(Ga\text{-}In)}$ *vs.* the temperature the semi-galvanic cell (2) was used.

$$(-)\ Mo_{(s)}\ La,\ (U)\ |\ \text{molten salt},\ La^{3+},\ (U^{3+})\ ||\ \text{molten salt}\ |\ C_{(s)},\ Cl_{2(g)}\ (+) \quad (1)$$

$$(-)\ La,\ U\ (\text{alloy})\ |\ \text{molten salt},\ La^{3+},\ (U^{3+})\ ||\ \text{molten salt}\ |\ C_{(s)},\ Cl_{2(g)}\ (+) \quad (2)$$

In this case the following scheme was used. After short polarization leading to formation of Me-Ga-In alloy the open circuit potentiometry measurements were carried out. The value of horizontal plateau is quasi-equilibrium potential of alloy. The concentration of La (U) in alloy was less than 0.4 wt. %. In this case the cathode was a liquid gallium-indium eutectic placed in a crucible of berlox. Lanthanum (uranium) containing alloys were prepared by cathodic deposition of La^{3+} (U^{3+}) ions from the chloride melt on Ga-In cathode (dilute solution) directly in the experimental cell before commencing the electromotive force (EMF) measurements. The counter electrode consisted of a 3 mm vitreous carbon rod (SU - 2000). The Cl^{-}/Cl_2 reference electrode was used in experiments. It standard construction is described earlier in details [31,38].

Variation of the apparent standard electrode potentials of metals and alloys as a function of the temperature were fitted by using software Origin Pro version 7.5.

The lanthanum (uranium) concentration in chloride salt was determined by taking samples from the melt which were dissolved then in nitric acid solutions and analysed by ICP-MS.

Lanthanum (uranium) containing alloys were washed with water followed by ethanol and then dried at room temperature. To determine the alloys composition they were quantitatively dissolved in a mixture of nitric and hydrochloric acids and the resulting solutions analyzed by ICP-MS.

3. Results and discussion

The values of the apparent standard redox potentials of $E^{*}{}_{La^{3+}/La}$ ($E^{*}{}_{U^{3+}/U}$) were calculated by Nernst equation (3)

$$E_{Me(III)/Me} = E^{*}_{Me(III)/Me} + \frac{RT}{nF}\ln C_{Me^{3+}}, \quad (3)$$

$$\text{where} E^{*}_{Me(III)/Me} = E^{\circ}_{Me(III)/Me} + \frac{RT}{nF}\ln f_{Me^{3+}}, \quad (4)$$

where $E_{Me(III)/Me}$ is the quasi-equilibrium potential of the system, V; $E^{*}_{Me(III)/Me}$ is the apparent standard redox potential of the system, V; n is the number of exchange electrons; $C_{Me^{3+}}$ is the concentrations of lanthanum (uranium) ions in mole fraction, $f_{Me^{3+}}$ is an activity coefficient.

Variation of the apparent standard redox potentials of the couples La^{3+}/La (U^{3+}/U) as a function of the temperature are presented in Fig. 1. The experiment data were fitted to the following equations (5) and (7) at the temperature range 723–823 K and they are in a good agreement with equations (6) [26] and (8) [32], respectively.

$$E^{*}_{La(III)/La} = -(3.731 \pm 0.004) + (7.3 \pm 0.6) \cdot 10^{-4} \cdot T \pm 0.004, V \quad (5)$$

$$E^{*}_{La(III)/La} = -3.712 + 8.267 \cdot 10^{-4} \cdot T, V \quad (6)$$

$$E^{*}_{U(III)/U} = -(3.005 \pm 0.004) + (5.9 \pm 0.2) \cdot 10^{-4} \cdot T \pm 0.003, V \quad (7)$$

$$E^{*}_{U(III)/U} = -2.98 + 6.59 \cdot 10^{-4} \cdot T, V \quad (8)$$

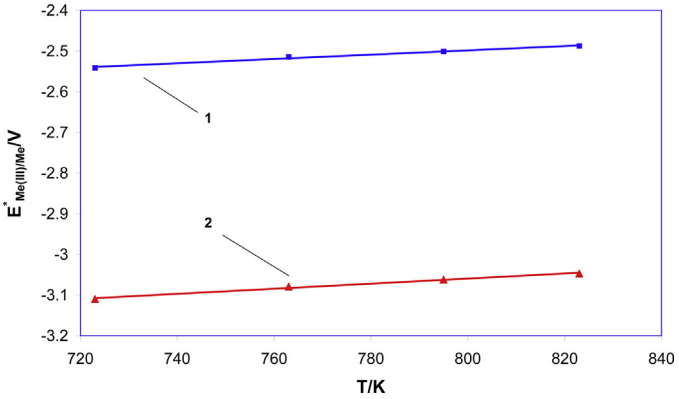

Figure 1. Variation of the apparent standard redox potential $E^{*}_{U(III)U}$ (1) and $E^{*}_{La(III)La}$ (2) vs. Cl^{-}/Cl_2 as a function of the temperature in fused LiCl-KCl-$MeCl_3$ melt. Concentration of $LaCl_3$ in solvent – 1.64 wt.%; concentration of UCl_3 in solvent – 1.47 wt.%.