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Thermodynamics of La and U and the separation factor of U/La in fused Me(Ga-40 wt.% In)/3LiCl-2KCl system

Valeri Smolenski [a, b, *], Alena Novoselova [a, b], Vladimir A. Volkovich [b]

[a] Institute of High-Temperature Electrochemistry UB RAS, 20 Akademicheskaya St., 620137, Ekaterinburg, Russia
[b] Department of Rare Metals and Nanomaterials, Institute of Physics and Technology, Ural Federal University, 21 Mira St., 620002, Ekaterinburg, Russia

HIGHLIGHTS

- Thermodynamic properties of La and U in the ternary La-Ga-In and U-Ga-In alloys were determined.
- During separation U is accumulating in the metallic phase and La in the salt phase.
- Efficient separation factor of An from Ln in liquid metal/molten salt system was observed.

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ABSTRACT

Separation of lanthanides and actinides can be achieved in a unique "molten chloride – liquid metal" system. Electrode potentials were recorded vs. Cl^-/Cl_2 reference electrode and the temperature dependencies of the apparent standard potentials of La-(Ga-In) and U-(Ga-In) alloys were determined. Thermodynamic properties and separation factor of lanthanum and uranium were calculated. The obtained data show the perspective for using this system in future innovation method for recovery of nuclear waste.

1. Introduction

Non-aqueous (pyrochemical) technologies for reprocessing of spent nuclear fuel (SNF) of atomic power plants stimulate a growing interest due to the necessity to provide safety and efficiency of nuclear fuel cycle. These technologies have a number of significant advantages as compared to aqueous (hydrometallurgical) technology, which include a drastic cut of radioactive wastes, engineering support of the fissile material nonproliferation principle and cheapening of SNF reprocessing [1–3]. The major steps of the pyrochemical technology include electrorefining or reductive extraction in a "molten chloride – liquid metal" system for recovering actinides, including the minor actinides, from the spent metallic or nitride nuclear fuels and high level radioactive wastes [4,5]. A strategy termed "Partitioning and Transmutation" (P&T) is currently being developed in several countries. The primary goal is achieving the maximum possible reduction of the nuclear waste radiotoxicity in the back end of the fuel cycle, offering a reduced heat load and more compact repository per kilogram uranium.

Lanthanide elements constitute an important group of fission products present in spent nuclear fuel of thermal and fast reactors. Information concerning the behavior and properties of these elements in molten salts is important for developing methods of pyrochemical reprocessing of SNF. The efficiency of separating lanthanide (Ln) and actinide (An) elements was proposed by the following sequence of the low-melting metals: Ga > Sn > Bi > In > Zn > Cd. The estimation of thermodynamic properties of liquid metals show that from all low melting metals gallium is most efficient in separating of Ln from An [6]. In this case binary and ternary molten alloys based on Ga can be used to lower the operation temperatures of metallic alloys and to improve some of its

* Corresponding author. Institute of High-Temperature Electrochemistry UB RAS, 20 Akademicheskaya St., 620137, Ekaterinburg, Russia.
E-mail address: smolenski.valeri@gmail.com (V. Smolenski).

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technical properties. Also the vapor pressure of gallium-indium systems, in particular, is very low even at relatively high temperatures. These features can simplify technological process and engineering design requirements.

Behavior of lanthanum has so far been studied in binary systems, La-Ga [7] and La-In [8] and the behavior of uranium – in binary systems, U-Ga [9] and U-In [10]. Thermodynamic properties of lanthanum and uranium and the separation factor (SF) of U/La in liquid eutectic gallium-indium alloy/molten salt system was also studied [11]. In this citation, the activity coefficients of lanthanum and uranium were determined in the ternary La-(Ga-20 wt.% In) and U-(Ga-20 wt.% In) alloys between 723 and 823 K.

In the present study the base thermodynamic properties of lanthanum (uranium) and the separation factor of U/La were determined on Ga-40 wt.% In alloy with the goal to understand the influence of composition of alloy on different properties of Ga-In system.

2. Experimental

The experiments were carried out at 723–823 K under dry argon atmosphere in an electrochemical cell with a two electrode setup. The design of cell is described earlier in details [12]. The electrochemical measurements were performed employing an AUTOLAB 302N potentiostat-galvanostat controlled by NOVA 1.11 software. Salt and metal mixtures of the required compositions were prepared from the individual components, LiCl (Aldrich, 99.99%), KCl (99.9%, certified purity), $LaCl_3$ (99.9%, certified purity), Ga (99.99%, certified purity), In (99.98%, certified purity). The following galvanic cell was used for measuring the electrode potentials of alloys, $E^{**}_{Me(Ga-In)}$:

$$(-)\ \mathrm{Me(Ga\text{-}40\ wt.\%\ In)}\ |\ \mathrm{3LiCl\text{-}2KCl,\ Me(III)}\ ||\ \mathrm{3LiCl\text{-}2KCl}\ |\ \mathrm{C_{(s)},\ Cl_{2(g)}}\ (+) \quad (1)$$

The concentration of La (U) in alloys was less than 0.4 wt. %. In this case the cathode was a liquid gallium-indium mixture placed in a crucible of BeO. 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 measurements. The Cl^-/Cl_2 reference electrode was used in experiments. It standard construction is described earlier in detail [13].

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

3. Results and discussion

The value of the apparent standard redox potential of couple Me(III)/Me were determined by potentiometry at zero current. The technique of the method were described earlier and written in details [11]. The values of $E^*_{La(III)/La}$ and $E^*_{U(III)/U}$ were calculated by Nernst equation (2):

$$E_{Me(III)/Me} = E^*_{Me(III)/Me} + \frac{RT}{3F}\ln C_{Me(III)} \quad (2)$$

where

$$E^*_{Me(III)/Me} = E^0_{Me(III)/Me} + \frac{RT}{3F}\ln f_{Me(III)} \quad (3)$$

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

Experimental data of the equilibrium potentials of the couples La(III)/La and U(III)/U vs. Cl^-/Cl_2 in fused 3LiCl–2KCl eutectic at different concentrations and temperatures are presented in Table 1. There are two points of view about the dependence of the activity coefficients vs. concentration in dilute molten salts. From one point of view the activity coefficients of the solute species Me^{n+} in solutions are constant at concentrations below $(3–5)\cdot10^{-2}$ mole fraction within the error of the experiments [13–19]. From another point of view this dependence has an extreme character [20,21]. The author's of this manuscript adhere to the first point of view in the subsequent discussion. Variation of the apparent standard redox potentials of the couples La^{3+}/La (U^{3+}/U) as a function of the temperature were fitted by the following equations using an Origin Pro version 7.5 software:

$$E^*_{La(III)/La} = -(3.731\pm0.004) + (7.3\pm0.6)\cdot10^{-4}\cdot T\pm0.004 \quad V \quad (4)$$

$$E^*_{U(III)/U} = -(3.005\pm0.004) + (5.9\pm0.2)\cdot10^{-4}\cdot T\pm0.003 \quad V \quad (5)$$

The values of the apparent standard redox potential of Me(Ga-In) alloys were calculated by Nernst equation (6)

$$E_{Me(alloy)} = E^0_{Me(III)/Me} + \frac{RT}{3F}\ln\frac{a_{Me^{3+}}}{a_{Me(alloy)}} \quad (6)$$

or

$$E_{Me(alloy)} = E^0_{Me(III)/Me} + \frac{RT}{3F}\ln\frac{C_{Me^{3+}}\cdot f_{Me^{3+}}}{x_{Me(alloy)}\cdot\gamma_{Me(alloy)}} \quad (7)$$

The potentiometric method at zero current was the following. After preparing of the alloys of the specified composition, the potential–time dependences were recorded at different temperatures. The potential value of the horizontal part of the curve corresponded to the quasi equilibrium potential of the alloy. For dilute solutions of Me in alloys, the activity coefficients are constant [6]. To characterize the electrochemical behavior of the alloy, an apparent standard potential of the alloy, $E^{**}_{Me(alloy)}$, was used [6]:

$$E_{Me(alloy)} = E^{**}_{Me(alloy)} + \frac{RT}{3F}\ln\frac{c_{Me^{3+}}}{x_{Me(alloy)}} \quad (8)$$

where $E_{Me(alloy)}$ is the equilibrium potential of the alloy, V; $E^{**}_{Me(alloy)}$ is the apparent standard potential of the alloy, V; n is the number of exchange electrons; $C_{Me^{3+}}$ is the concentrations of metal ions in solvent in mole fraction; $x_{Me(alloy)}$ is the concentrations of metal atoms in alloy in atomic fraction.

Variation of the apparent standard potential of Me(Ga-40 wt.% In) alloys as a function of temperature were fitted to the following equations using an Origin Pro version 7.5 software and presented in Fig. 1: