Thermodynamics of separation of uranium from neodymium between the gallium-indium liquid alloy and the LiCl-KCl molten salt phases

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ABSTRACT

This work presents the electrochemical study of neodymium and uranium compounds in fused LiCl-KCl eutectic *vs.* Cl$^-$/Cl$_2$ reference electrode in the temperature range 723-823 K on liquid gallium-indium eutectic alloy. The activity, solubility and the activity coefficients of neodymium were calculated. The separation factor of uranium from neodymium on gallium-indium eutectic alloy was determined. The obtained data show the perspective of used this system in future innovation method for recovery of nuclear waste.

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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 so far to separate the actinides from the fission products arising from nuclear energy production: hydrometallurgical and pyrometallurgical processes.

Fast neutron reactors allow more efficient to use uranium resources. In addition this type of reactors is capable of burning long lived actinides (including those accumulated in thermal reactors spent fuel) thus reducing radioactivity of nuclear wastes. Application of fast reactors results in considerable increase of fuel burn up and, if the reactor is operated as breeder, reproduces fissile materials. At present non-aqueous pyrochemical methods employing molten salts and liquid metals are developed for reprocessing spent nuclear fuels (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 a 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 Nd^{3+} ions in molten chlorides and thermodynamic properties of the reaction NdCl$_2$ + $^1/_2$Cl$_2$ = NdCl$_3$ in molten chlorides were studied in details [26]. The mechanism of the electrochemical reduction occurs through two consecutive steps: Nd^{3+} + ē → Nd^{2+} and Nd^{2+} + 2ē → Nd. The chemical stability of Nd^{2+} ions in fused chloride melts is not stable at temperatures above 810–840 K. Apparent standard redox potentials of the couple $E^*_{Nd^{3+}/Nd^{2+}}$ were determined and the base thermodynamic properties of the reaction NdCl$_2$ + $^1/_2$Cl$_2$ = NdCl$_3$ were calculated [26]. Stationary and transient investigations of the behavior of Nd^{3+} and U^{3+} ions in molten chlorides on liquid Ga-In alloys are unknown.

The estimation of thermodynamic properties of liquid metals [27] show that from all low melting metals gallium is most efficient in separating of lanthanides from actinides (*e.g.* system La/U).
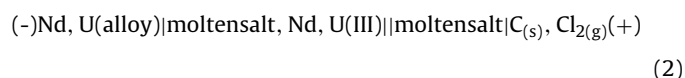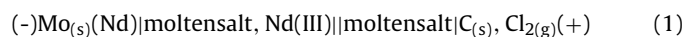
Binary and ternary eutectic mixtures can be used to lower melting point of metallic alloys and thus the operation temperatures. Gallium-indium system offers one of the lowest melting eutectics with the melting point around 289 K [28]. Vapor pressure of the metallic phase is another important factor to 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. [29]. 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. Behaviour of neodymium has so far been studied only in binary systems, Nd-Ga and Nd-In [28,29] and the behaviour of uranium–in binary systems, U-Ga [30] and U-In [31]. There is no information on thermodynamic properties of neodymium and on separation factor of uranium from neodymium on metallic alloys containing low melting metals.

In the present study the base thermodynamic properties of neodymium and the separation factor of uranium from neodymium was determined in 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 $E^*_{Nd^{3+}/Nd}$ *vs.* the temperature the semi-galvanic cell (1) was used. The concentration of neodymium (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 cm². For obtaining the dependence of the apparent standard redox potential of alloy, $E^{**}_{Nd(In-Ga)}$ or $E^{**}_{U(In-Ga)}$ *vs.* the temperature the semi-galvanic cell (2) was used.

$$(-)Mo_{(s)}(Nd)|moltensalt, Nd(III)||moltensalt|C_{(s)}, Cl_{2(g)}(+) \qquad (1)$$

$$(-)Nd, U(alloy)|moltensalt, Nd, U(III)||moltensalt|C_{(s)}, Cl_{2(g)}(+) \qquad (2)$$

The concentration of Nd (U) in alloy was less then 0.8 wt. %. In this case the cathode was a liquid gallium-indium eutectic placed in a crucible of berlox. Neodymium containing alloys were prepared by adding required amount of metallic neodymium to the Ga-In alloy (saturated solution) or by cathodic deposition of neodymium(III) ions from the chloride melt on Ga-In cathode (dilute solution) directly in the experimental cell before commencing the electromotive force (EMF) measurements. Uranium containing alloys were prepared by cathodic deposition of uranium (III) ions from the chloride melt on Ga-In cathode (dilute solution) directly before measurements. The counter electrode consisted of a 3 mm vitreous carbon rod (SU - 2000). The Cl⁻/Cl₂ reference electrode was used in experiments. It standard construction is the following. The quartz tube with porous membrane in the bottom and molten solvent in it has the graphite tube for chlorine gas introduction into the system. The chlorine gas is bubbling through the melt during all experiment [32].
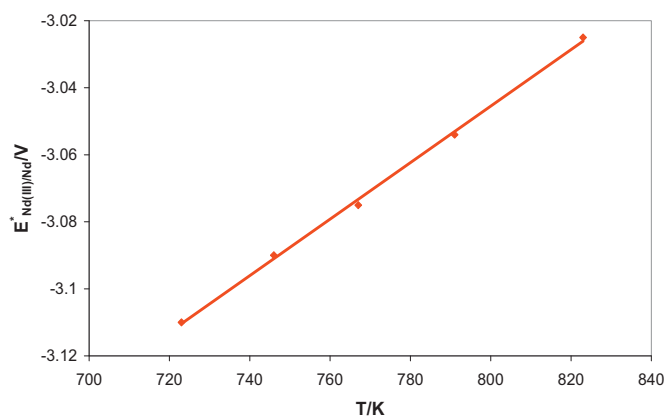

Fig. 1. Variation of the apparent standard redox potential $E^*_{Nd(III)/Nd}$ vs. Cl⁻/Cl₂ as a function of the temperature in fused LiCl-KCl-NdCl₃ melt. Concentration of NdCl₃ in solvent–1.78 wt.%.

The neodymium (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.

Neodymium (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 value of the apparent standard redox potential was determined by potentiometry at zero current. The essence of this method is the following. The inert molybdenum electrode was polarized at potentiostatic conditions for a short time and after deposition a small amount of metal neodymium on the surface of working electrode the dependence of potential-time was fixated. The value of horizontal plateau is a quasi-equilibrium potential of the couple Nd(III)/Nd.

The value of the apparent standard redox potential of the couple Nd(III)/Nd was calculated by Nernst equation (3)

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

where

$$E^*_{Nd(III)/Nd} = E^\circ_{Nd(III)/Nd} + \frac{RT}{nF} \ln f_{Nd^{3+}} \qquad (4)$$

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

Variation of the apparent standard redox potential of the couple Nd³⁺/Nd as a function of the temperature is presented in Fig. 1. The experiment data were fitted to the following equation using Software Origin Pro version 7.5 and is in a good agreement (eq. 6 and 7) with the literature [33,34], respectively.

$$E^*_{Nd(III)/Nd} = -(3.750 \pm 0.005) + (8.82 \pm 0.12) \cdot 10^{-4} T \pm 0.003 V \qquad (5)$$

$$E^*_{Nd(III)/Nd} = -3.554 + 6.4 \cdot 10^{-4} \cdot TV \qquad (6)$$

$$E^*_{Nd(III)/Nd} = -3.772 + 9.1 \cdot 10^{-4} \cdot TV \qquad (7)$$