



Electrochemical behaviour of terbium in the eutectic LiCl-KCl in Cd liquid electrodes.- Evaluation of the thermochemical properties of the TbCd_x intermetallic compounds



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ABSTRACT

The electrode reaction of Tb(III)/Tb couple in the eutectic LiCl-KCl, at Cd liquid electrodes (i.e a Cd pool and a Cd coated W electrodes) was investigated in the temperature range of 673–823 K. In both electrodes, the electrochemical reduction of Tb(III) was observed at less cathodic potential values than at the surface of an inert W electrode, due to the decrease of Tb activity in the metal phase.

Cyclic voltammetry, using a Cd bulk electrode, suggest a quasi-reversible behaviour of the system Tb(III)/Tb_(dissolved in liquid Cd), and the values of the kinetic parameters, k^0 and α , as well as the reversible half wave potential, $E_{1/2}^r$, have been obtained. The differences between the equilibrium potential adopted by a Tb electrode and the $E_{1/2}^r$ observed with the same Tb(III) solution at the Cd pool electrode, were used to calculate approximate values of the excess Gibbs energy change of Tb in liquid metal, and hence the activity coefficient of Tb in Cd.

The formation of intermetallic compounds was also studied. Electromotive force, *emf*, measurements for five intermetallic compounds in two-phase coexisting states were carried out using a Cd coated tungsten electrode. The activities and relative partial molar Gibbs energies of Tb were obtained for TbCd₆, TbCd_{45/11}, TbCd₃, TbCd₂ and TbCd. The formation energy of each intermetallic compound, and the global formation constants were also calculated. The linear dependence of the Gibbs free energies with temperature yields to the enthalpies and entropies of formation of the five intermetallic compounds.

Analysis of the samples after electrolysis runs by scanning electron microscopy (SEM) with energy dispersive X-ray allowed the identification of TbCd₆, TbCd₃, TbCd₂ and TbCd.

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1. INTRODUCTION

A considerable effort is underway in the nuclear industry to minimise the potential impact of hazardous radioactive spent-fuel on the environment. Proposed solutions range from reprocessing to direct disposal in a deep geologically-stable repository. The main objectives for a closed fuel cycle scenario are: i) to recover all the actinides (Ans) for recycling or destruction, ii) to ensure sufficient decontamination between Ans and fission products (FPs), iii) to generate the minimum of ultimate waste flows and iv) to have suitable confinement of process wastes [1]. In this way, partitioning and transmutation (P&T) of Minor Actinides (MAs) and Long-Lived Fission Products (LLFP) arising out of the back-end

of the fuel cycle would be one of the key-steps in any future sustainable nuclear fuel cycle [1,2]

Pyrochemical separation methods, using molten chloride or fluoride electrolyte systems, would form a critical stage of P&T by recovering long-lived elements and thus reducing the radio-toxicity and volume of the nuclear wastes [2]. To this end, research and development is needed for molten salt electrorefining, electroextraction with inert and reactive cathodes, as well as reductive extraction process that are foreseen as partitioning methods for irradiated nuclear fuel [2–11].

Our team has been engaged in a research program in which a two-step process is foreseen in molten chlorides, corresponding to (i) the selective extraction of Ans and (ii) the extraction of Lns for decontamination of the salt. Our studies are devoted to the acquisition of fundamental data of Lns to allow conceptual design and assessment of reprocessing processes involving as separation steps electrolytic extraction via inert (W) and reactive liquid

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(Cd or Bi) or solid Al cathodes, and oxide selective dissolution/precipitation.

In the present paper, the electrode reactions of terbium, a heavy lanthanide, in a liquid Cd pool electrode and a Cd coated W electrode, was investigated and compared with the case of an inert cathode. Being the aims of the work: (i) to find an easy way of determining the activity coefficients of Tb in liquid metal, and (ii) to calculate the Gibbs free energies of formation of the different $TbCd_x$ intermetallic compounds by means of electrochemical techniques. The paper describes the methods used as well as the obtained results.

2. EXPERIMENTAL

2.1. General features

Storage of all chemicals and electrolytic bath preparation, a mixture of LiCl-KCl with the eutectic composition (Sigma Aldrich 99.99%), were handled in a MBraun glove box in purified Ar atmosphere where the oxygen content and H_2O levels were maintained below 2 ppm. The electrolyte, introduced in a high purity alumina crucible placed in a cylindrical quartz cell, was fused under vacuum during 8 h and then raised to atmospheric pressure using dry argon (99.999%, Air Liquide). The cell was heated using a tubular furnace connected to a West 3300 programmable device, and the working temperature was controlled with a nickel-chromium thermocouple with an accuracy of ± 2 K.

Purification of the melt was carried out by bubbling $HCl(g)$ for 30 minutes, being removed the residual HCl by bubbling Ar. All electrochemical experiments were performed in the purified eutectic mixture under a dry Ar atmosphere.

Solutions of Tb(III) and Cd(II) were prepared by direct additions of anhydrous $TbCl_3$ and $CdCl_2$ (Sigma Aldrich 99.99%). In order to avoid Tb_2O_3 and $TbOCl$ formation, $HCl(g)$ was bubbled every day prior to the determinations.

The total concentration of dissolved Tb(III) was calculated by ICP-AES analysis of melt samples, which were taken by means of a Pyrex tube provided with a fritted glass of porosity 4.

2.2. Electrochemical apparatus and electrodes.

The reference electrode consisted of a silver wire (1 mm diameter) dipped into a silver chloride solution (0.75 mol kg^{-1}) in the LiCl-KCl molten mixture, contained in a Pyrex tube.

Different working electrodes have been used: (i) a liquid Cd bulk electrode ($S \approx 0.6 \text{ cm}^2$), and (ii) a tungsten wire of 1.0 mm diameter (Sigma Aldrich 99.99%) coated with Cd(0). As counter electrodes, a glassy carbon rod (Sofagel) of 3 mm diameter and a 1.5 mm diameter tungsten wire (Alfa Aesar 99.95%) have been used.

The liquid Cd pool electrode was prepared by placing some granules of Cd (99.999%; Sigma Aldrich) in a J shaped Pyrex tube, which was immersed in the LiCl-KCl melt. Contact was established by using a tungsten wire of 1 mm in diameter immersed in the Cd phase through the Pyrex tube. We would like to remark that even if the liquid metal surface was hemispherical, we are not in spherical diffusion conditions. The latter would suppose that the liquid metal would flush on top of the J vessel. Subsequently, the results obtained on this electrode have been interpreted adopting the planar diffusion model.

The electrochemical measurements were performed with: (i) a PAR EG&G Model 273A potentiostat/galvanostat controlled by a computer using the EG&G M270 software package and (ii) an Autolab PGSTAT 320N potentiostat/galvanostat controlled by the research software NOVA 1.10.

Samples of intermetallic compounds were prepared by electrolysis using a Cd coated W wire of 1 mm diameter as cathode, and a W wire of 1.5 mm diameter as anode. After electrolysis, samples were immersed in anhydrous ethylene glycol (sigma Aldrich) to remove chloride salts, and washed with acetone. The deposits were analyzed by scanning electron microscopy (SEM, FEI Model Quanta 200F) and energy dispersive spectroscopy (EDAX, SDD Apolo).

3. RESULTS AND DISCUSSION

3.1. Electrode reactions of Tb(III)/Tb system in the reactive Cd pool electrode.

Fig. 1 curve (1), blue line, shows an example of the cyclic voltammograms obtained with a solution of $TbCl_3$ in the eutectic LiCl-KCl at a liquid Cd bulk electrode. The red dotted curve (2) shows the electrochemical spectra obtained at the interface between the LiCl-KCl melt and liquid Cd in the absence of $TbCl_3$. The cathodic limit of the voltammogram is attributed to the Li deposition in liquid Cd metal [6], whereas the anodic one corresponds to the anodic dissolution of the liquid Cd electrode.

Another cyclic voltammogram, grey curve (3), registered with the same $TbCl_3$ solution in the eutectic LiCl-KCl on a W electrode has also been represented in Fig. 1, allowing the comparison with the liquid substrate. The W electrode has been chosen because no alloys exist for the W-Tb binary systems.

As we have reported previously [12], when the substrate is an inert material (i.e. W), the reaction proceeds as one deposition/dissolution mechanism:



On the contrary, for the Cd pool electrode, the voltammogram consist of a cathodic wave A^c , associated with a well-defined anodic one A^a , at less cathodic potential values than those obtained at the inert electrode, and with the expected shape for a soluble-soluble electrochemical exchange. Therefore, the waves A^c/A^a can be attributed to the deposition of Tb in liquid Cd, and the oxidation of Tb dissolved in Cd respectively.



The potential shift of the electrochemical system in the positive direction compared with the reduction potential $Tb(III)/Tb$ at the inert electrode, it is due to a lowering of the activity of the dissolved Tb metal in the Cd phase as described in equation (3)

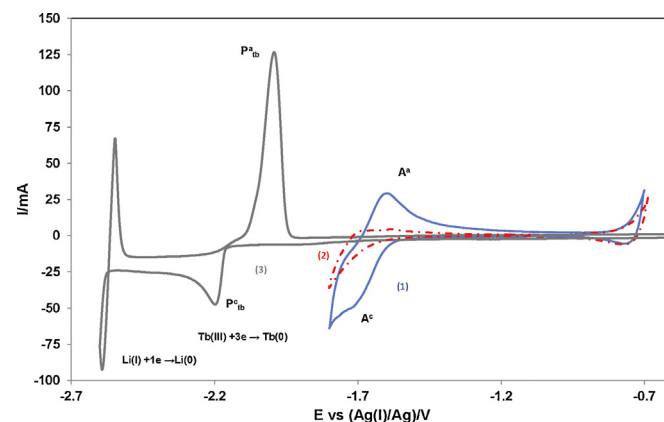


Fig. 1. Cyclic voltammograms for the reduction of a $TbCl_3$ solution in the eutectic LiCl-KCl ($C_0 = 1.15 \times 10^{-4} \text{ mol cm}^{-3}$) at a Cd pool, curve (1), and a W electrode, curve (3). Curve (2) shows the electrochemical spectra obtained at the interface between the LiCl-KCl melt and liquid metal in absence of $TbCl_3$. Scan rate: 0.075 V s^{-1} ; temperature 723 K.

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