Journal of Electroanalytical Chemistry 642 (2010) 150–156

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Electrochemical behaviour of dysprosium(III) in LiF–CaF_2 on Mo, Ni and Cu electrodes

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ARTICLE INFO

Article history:
Received 8 December 2009
Received in revised form 29 January 2010
Accepted 1 March 2010
Available online 6 March 2010

Keywords:
Molten fluorides
Dysprosium
Cyclic voltammetry
Square wave voltammetry
Surface alloys

ABSTRACT

The electrochemical behaviour of dysprosium(III) was investigated in the LiF–CaF_2 eutectic mixture on molybdenum, nickel and copper electrodes in the 840–930 °C temperature range using cyclic voltammetry, square wave voltammetry and chronopotentiometry. On Mo electrode, the study showed that Dy(III) ions were reduced into Dy metal in a one-step diffusion-controlled process exchanging three electrons: $\mathrm{Dy(III)} + 3e^- \leftrightarrow \mathrm{Dy}$. The diffusion coefficients verify the Arrhenius law, allowing the activation energy to be calculated. The study of the electrochemical reduction of Dy(III) ions on reactive electrodes (Ni, Cu) first by cyclic voltammetry showed that the reduction potential of Dy(III)/Dy on reactive electrodes was observed at more positive values than those on inert electrode and then open-circuit chronopotentiometry put into evidence the formation of intermetallic compounds at more anodic potentials than pure dysprosium. Preparation of alloys layers was finally carried out by intentiostatic electrolyses at underpotential compared to the pure metal deposition; SEM observations of the layer allowed the most stable compounds prepared by this way to be identified.

1. Introduction

Partitioning and Transmutation (P&T) of long-lived fission products and minor actinides are considered as one of the future options for nuclear waste management. Up to now, nuclear industries consider mainly hydrometallurgical methods such as the PUREX process for spent fuel treatment [1]. An alternative route should be the use of "dry" pyrochemical separation methods in non aqueous solvents. The separation processes by electrodeposition from molten salts appear to be acknowledged in all networks based on the nuclear of future. Compared with aqueous solvents, the choice of molten salts, such as alkali fluorides, is based on their relevant solvent properties. For electrochemical applications: larger electrochemical window, higher electrodeposition rates and better characteristics of the deposits [2,3]. Thanks to these advantages, pyrochemical reprocessing becomes more important for the implementation of the P&T programs to decrease the amount and long-term hazards of nuclear wastes.

In the frame of research works realized in our laboratory for establishing appropriate conditions to separate actinides (An) from lanthanides (Ln) and other fission products (FP) [4–7] in molten fluorides media, we plane to investigate on the intrinsic electrochemical parameters of all the elements concerned in order to obtain the background data relevant for the future An–Ln separation and extraction process in these media. In particular we observed that, in most cases, the Ln elements cannot be extracted completely from the solvent as pure metals on an inert electrode, because their equilibrium potential is too closed from the solvent wall, whereas we obtained almost 100% for the extraction rate of Nd and Gd on a reactive electrode where the metal is yielded in alloyed form [8].

In the present article, we study the electrochemical behaviour of dysprosium (which is one of the Ln produced in nuclear reactors) in DyF_3–LiF–CaF_2 for examining the possibilities of extraction from nuclear wastes either in pure state or alloyed one with a reactive cathode. A variety literature is available relating to the dysprosium in molten salts and often reports results of electro reduction of Dy(III) both on inert and reactive cathodes. Besides, the electro reduction pathway is controversial, about whether the intermediate Dy(II) participates or not to the electrode process. However the most noticeable contribution concerns the study of the reduction mechanism of Dy(III) ions by Castrillejo et al. [9] where the authors found a two-steps reduction mechanism in LiCl–KCl–$DyCl_3$ system in the 400–550 °C temperature range on W electrode as:

$$\mathrm{Dy(III)} + 1e^- \leftrightarrow \mathrm{Dy(II)} \quad (1)$$

$$\mathrm{Dy(II)} + 2e^- \leftrightarrow \mathrm{Dy(0)} \quad (2)$$

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doi:10.1016/j.jelechem.2010.03.002

The authors also investigate the formation of $DyAl_3$ alloy using potentiostatic electrolysis on aluminium reactive electrode.

Elsewhere, Chang et al. [10] proposed, in the same chloride medium, an electrochemical reduction in a one-step process exchanging three electrons, in agreement with Konishi et al. [11–14] who measured, in the same system at 500 °C, a reduction potential of 0.47 V vs. Li^+/Li Ref. [11]. Furthermore, they have evaluated, on Fe and Ni electrodes, the equilibrium potential of Fe–Dy and Ni–Dy compounds and calculated their thermodynamic properties. Always in chlorides salts, a spectroscopic study of some trivalent lanthanides, carried out by Fujii et al. [16], evidenced the dependence of the $DyCl_6^{3-}$ complex geometry on temperature and nature of the salts. Zeng et al. [15] performed a similar study in $Li2CO_3^-$ K_2CO_3 mixture at 377 °C on Ni electrode.

The separation of FP by phosphate precipitation in molten chlorides was studied by Volkovich et al. [17] in the 550–750 °C temperature range. The effect of the PO_4^{3-} ions addition on the distribution coefficient of Dy(III) and other fission products has been examined.

The purpose of the present article is to determine the electrochemical behaviour of $LiF–CaF_2–DyF_3$ system on different substrates: (i) inert electrode (Mo) in order to study the electrodeposition of Dy metal, (ii) reactive electrodes (Ni, Cu) for the formation of intermetallic compounds. The experimental techniques used were cyclic voltammetry, square wave voltammetry, chronopotentiometry and open-circuit chronopotentiometry.

2. Experimental

The cell consisted of a vitreous carbon crucible placed in a cylindrical vessel made of refractory steel and closed by a stainless steel lid cooled by circulating water. The inner part of the cell walls was protected against fluoride vapours by a graphite liner. The experiments were performed under an argon (less than 5 ppm O_2) atmosphere, previously dehydrated and deoxygenated using a purification cartridge (Air Liquide). The cell was heated using a programmable furnace and the temperatures were measured using a chromel–alumel thermocouple.

The electrolytic bath consisted of a eutectic $LiF–CaF_2$ (Merck 99.99%) mixture (79/21 M ratio). Before use, it was dehydrated by heating under vacuum (10^{-2} mbar) from ambient temperature up to its melting point (762 °C) for 48 h. Dysprosium ions were introduced into the bath in the form of pellets of dysprosium trifluoride, DyF_3 (Merck 99.99%).

Electrodes: molybdenum wire (1 mm diameter) was used as inert working electrode, nickel (1 mm diameter) and copper wires (1.2 mm diameter) were used as reactive electrodes. The area of the working electrode was determined after each experiment by measuring the immersion depth in the bath. The auxiliary electrode was a vitreous carbon (V25) rod (3 mm diameter) with a large surface area (2.5 cm^2). The potentials were referred to a platinum wire (0.5 mm diameter) immersed in the molten electrolyte, acting as a quasi-reference electrode $Pt/PtO_x/O^{2-}$ (QRE) with a potential remaining constant for a given low oxide content in the bath [18].

The electrochemical techniques used to the study of the electroreduction process of Dy(III) species (cyclic voltammetry, square wave voltammetry and chronopotentiometry), were performed with an Autolab PGSTAT 30 potentiostat/galvanostat controlled by computer using the GPES 4.9 software.

The cathode surface areas were examined after electrochemical reduction by Scanning Electron Microscopy (LEO 435 VP) with EDS probe (Oxford INCA 2000).

3. Results and discussion

3.1. DyF_3 electrochemical reduction mechanism on inert electrode

First, the dysprosium E-pO^{2-} diagram, plotted in Fig. 1 from HSC 5.1 software at 840 °C (1113 K) with all soluble species activities equal to 0.1 mol kg^{-1}, allows dealing with the following inquiries:

- For low oxide contents, only DyF_3 and Dy are observed. So, DyF_2 is not considered as thermodynamically stable; this result is in agreement with those obtained by Bratsch et al. [19]. According to this diagram, DyF_3 should be electrochemically reduced into Dy, so the only predicted reaction is:

$$DyF_3 + 3e^- \leftrightarrow Dy + 3F^- \tag{3}$$

This reaction occurs at lower cathodic potential than the solvent discharge ($Li^+ + e \leftrightarrow Li$). Consequently, Dy metal deposition was considered theoretically possible on inert electrode.

- At high O^{2-} ions activity (pO^{2-} < 2.8), DyF_3 precipitates into Dy_2O_3 stable oxide. So, to avoid its formation, the free oxide content in the bath must be kept at low values.

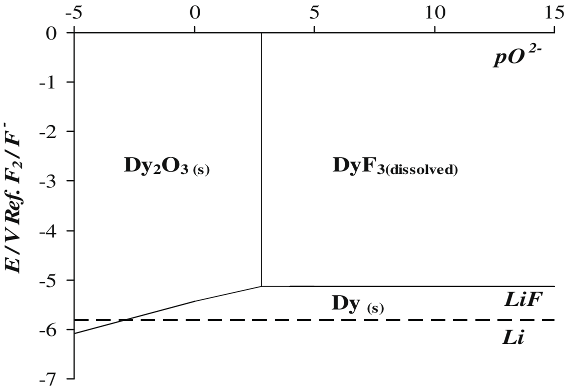

Fig. 1. E-pO^{2-} diagram made using HSC 5.1 software at 840 °C in the LiF–sCaF_2 melt and all soluble species activities equal to 0.1 mol kg^{-1}.

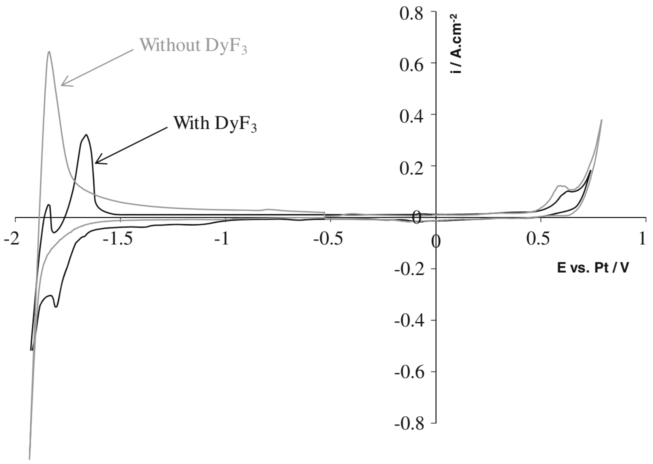

Fig. 2. Typical cyclic voltammogram of $LiF–CaF_2–DyF_3$ (9.4×10^{-5} mol cm^{-3}) system, compared with the one of $LiF–CaF_2$ at 100 mV s^{-1} and 840 °C. Working El.: Mo ($S = 0.4\ cm^2$); auxiliary El.: vitreous carbon; quasi-reference El.: Pt.