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Extraction of neodymium by direct reduction of NdOCl in molten calcium chloride

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ABSTRACT

The direct electrochemical extraction of neodymium using a modified (Fray-Farthing-Chen) FFC process is proposed in this article. In this modified FFC process, NdOCl, prepared from the reaction of Nd_2O_3 and $CaCl_2$ was used as the cathode and an yttria stabilized zirconia (YSZ) tube loaded with tin was used to separate the anode from the molten electrolyte. NdOCl reduction occurs in two steps: NdOCl to NdO and NdO to Nd, as determined by cyclic voltammetry. The diffusion coefficients of NdO^+ and oxygen ions were also calculated for each step. A cell voltage of 3.6 V was found to be sufficient to have a reduction of NdOCl to Nd metal.

1. Introduction

Neodymium production has increased due to the demand for Nd-Fe-B permanent magnets. However, neodymium oxide like the other rare earth oxides are amongst the most stable oxides known in nature and their reduction to a metal is often very difficult [1,2]. The electrolytic production of neodymium metal from neodymium oxide is considered an attractive method [3–5]. Morrice et al. for instance investigated the electrolytic preparation of neodymium metal from Nd_2O_3 [2]. The electrolysis was conducted in a thermal gradient cell in which the metal was electrowon in a high temperature zone and dripped down from a molybdenum rod cathode. The Fray-Farthing-Chen (FFC) process is a relatively new process which makes it possible to produce metals and alloys through direct electrochemical reduction of the respective oxides in fused salts [6]. In the FFC process, the oxide at the cathode is electroreduced, while the oxygen ions react with the carbon anode to form CO_2/CO. The use of a carbon anode, however, has some limitations. If the salt is electrolytically decomposed, the evolved chlorine gas can react with the carbon anode to form greenhouse gases like CCl_4 and C_2Cl_6. Moreover, CO_2 evolved during electrochemical reduction of oxides may dissolve in the melt and react at the cathode (See Eqs. (1) and (2)) leading to carbon contamination of the metallic product [7–9]. Moreover, the carbon that is formed may also lead to cell shorting.

$$CO_2 + O^{2-} = CO_3^{2-} \quad (1)$$

$$CO_3^{2-} + 4e^- = 3O^{2-} + C \text{ (on cathode)} \quad (2)$$

The use of a solid-oxide oxygen-ion-conducting membrane (SOM), in which an yttria stabilized zirconia (YSZ) tube is used as a membrane surrounding the anode and an oxide is used as cathode, is a promising way to produce metals [10–12]. In the SOM process, a YSZ tube separates the anode from the molten electrolyte and oxygen [13–15]. A voltage is applied to dissociate the metal oxide dissolved in the electrolyte, so that metal deposits at the cathode and oxygen ions are transported through the membrane to the anode [16]. Liquid silver, tin or copper contained at the bottom of the YSZ tube serves as the anode [17,18]. The SOM process avoids the carbon contamination problem.

In case of Nd production through the SOM process, the solubility of Nd_2O_3 is not more than 2.0 mol% in fluoride salts in the temperature range of 1050 °C to 1150 °C [19]. It is even less in molten $CaCl_2$ (the conventional electrolyte used in the FFC process) [1]. Moreover, Nd_2O_3 reacts rapidly with molten $CaCl_2$ to form an insoluble oxychloride (NdOCl) [20]. All this implies that Nd_2O_3 is not a good choice as cathode material for the FFC process or the SOM process.

In this article, we demonstrate the electroreduction of neodymium oxychloride to metallic Nd in molten $CaCl_2$. In this

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context, neodymium oxychloride, which is quite stable in the molten salt, was synthesized through the reaction between Nd_2O_3 and $CaCl_2$. The present work was undertaken to demonstrate the possibility to produce Nd through a 'modified' FFC process which used tubular YSZ membranes to protect the anode. The purpose is to investigate the electrodeoxidation processes taking place on the cathode and to elucidate the reduction mechanism of neodymium from neodymium oxychloride.

2. Experimental

2.1. Preparation of NdOCl

NdOCl can be prepared by reacting Nd_2O_3 with $NdCl_3$ at 830 °C in a gold crucible for 2 hours, the molar ratio of $NdCl_3/Nd_2O_3$ being >1 [21]. In our previous work, confocal scanning laser microscopy (CSLM) images show that Nd_2O_3 dissolves in $CaCl_2$ and forms insoluble NdOCl through reaction (3) [20]:

$$CaCl_2 + Nd_2O_3 = 2\ NdOCl + CaO\ (\Delta G^\circ = -10.3\ kJmol^{-1}\ at\ 850\,^\circ C) \quad (3)$$

Thermodynamically, NdOCl can be made by the reaction of $CaCl_2$ and Nd_2O_3 at 850 °C. The mixture of $CaCl_2$ and Nd_2O_3 (the $CaCl_2/Nd_2O_3$ molar ratio is 3.0) was heated to 850 °C. After the reaction completed, the salt batch was cooled to room temperature and washed with dilute hydrochloric acid (0.1 wt.%) to remove excess $CaCl_2$, CaO and $Nd(OH)_3$ where $Nd(OH)_3$ comes from the reaction of NdOCl and water. The product has a light-blue color after it was filtered and dried at 120 °C for 24 hours. Then, it was pressed at 15 MPa with a manual tablet press (10 mm in diameter and 2 mm in thick) and subsequently pressureless sintered at 1100 °C for 12 hours. The final products were analyzed by X-ray diffraction (Seifert 3003) and scanning electron microscopy (SEM, Philips XL30 FEG). The results are shown in Fig. 1a and b, respectively. The XRD data (Fig. 1a) indicates that the product is NdOCl (PDF-8-46). The apparent density was measured by the Archimedes method using deionized water to be about 78% of the theoretical density. The NdOCl is much more stable than Nd_2O_3 in molten $CaCl_2$ at 900 °C (see supporting information).

2.2. Electrolyte preparation

The solvent salts were prepared by the following procedure. $CaCl_2$ mixed with CaO (1.5 wt.%, for constant-voltage electrolysis) and Y_2O_3 (12.0 wt.%) was pre-dried under vacuum for 24 h at 300 °C. Subsequently, the mixture was melted at 900 °C in a high purity argon atmosphere (99.999%). A pre-electrolysis lasting two hours was performed between a Kanthal wire cathode and the SOM anode at a potential of 2.5 V to remove redox impurities. The details of this process have been described elsewhere [19].

2.3. Electrochemical experimental setup and procedure

A three electrode cell assembly was used for all the electrochemical measurements, shown in Fig. 2a. A metallic cavity electrode (MCE) shown in Fig. 2b was fabricated from a Mo foil (2.0 mm width and 1.0 mm thickness with circular through-holes, 1.0 mm in diameter), and it was used as a working electrode to record cyclic voltammograms (CVs) [22].

The MCE cavities were filled with NdOCl by pressing NdOCl powder repeatedly on both sides of the foil around the through-holes. An YSZ tube that is used as a membrane surrounding a 6 mm diameter graphite rod served as the counter electrode. A platinum wire (99.99%, 1.0 mm dia and 30 mm length) was used as pseudo-reference electrode. All the potentials for the electrochemical

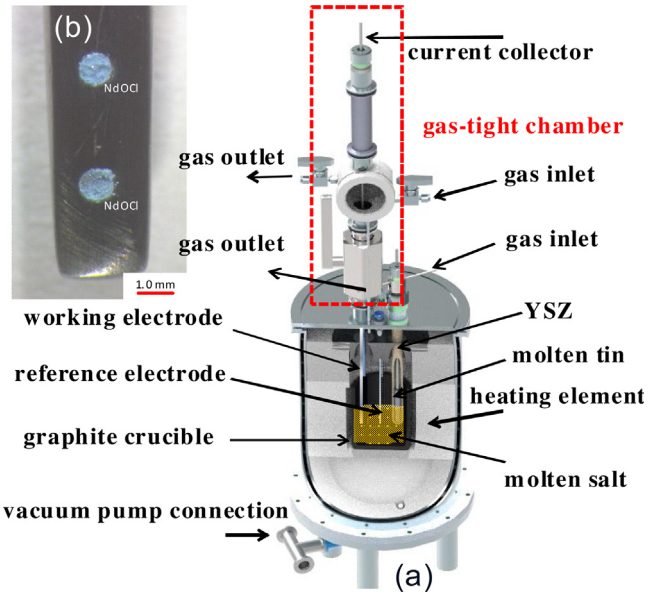

Fig. 2. (a) Schematic illustration of the experimental setup and electrode arrangement; (b) the metallic cavity electrode made from Mo foil.

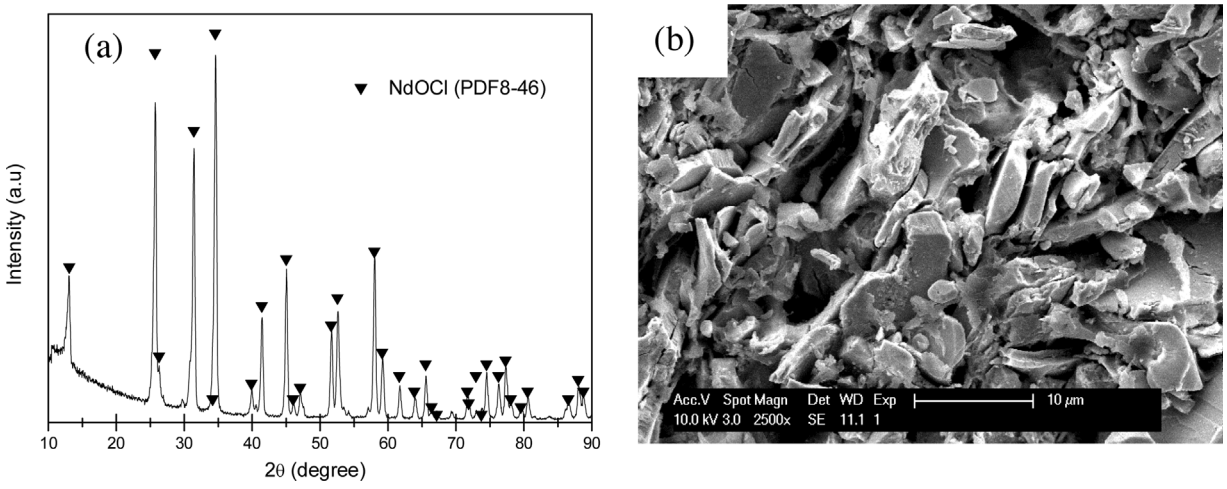

Fig. 1. (a) XRD pattern and (b) SEM of NdOCl after sintering at 1100 °C for 12 h.