

Dissolution Kinetics of Neodymium and Praseodymium Oxides in a PrF₃-NdF₃-LiF Melt.

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Abstract

A graphite probe was inserted into a 50 mol% each of NdF₃ and LiF melt containing oxides of Nd and Pr for voltammogram measurements during dissolution. Fast voltage sweeps (100 V/s) were applied to this graphite probe and the current responses were measured. As the oxide concentration in the diffusion layer towards the electrode depletes during current ramping, a passive layer is, at a certain point, formed on the probe, resulting in a rapid decrease of the current density. The voltage at this point was observed to be proportional to the concentration of the dissolved oxide. Melt samples taken during the measurements and analysed for oxygen content by LECO showed a very good correlation between the approximation based on the voltage at the critical current density and the concentration of dissolved oxides.

Introduction

Understanding the dynamics behind the dissolution of rare earth metal oxides in fluoride electrolytes is important for the efficient and environmental performance of the electrolytic reduction of these oxides. Furthermore, on-line monitoring of the oxide concentration in the fluoride melt will provide an opportunity for optimisation of the oxide feeding systems, thereby contributing to production efficiency. The concentration of rare earth metal oxides in their fluoride melts is an important prerequisite for smooth operations during the electrowinning process [1]. This is because fluoride melts deficient of oxide are observed to generate the perfluorocarbon (PFC) gases CF₄ and C₂F₆ that passivate the graphite anodes and consequently inhibit the electrolysis process [1, 2]. Furthermore, these perfluorocarbon (PFC) gases that are released as a result of oxide deficiency are climate gases with far higher global warming potential than carbon dioxide (CO₂). Thus, for efficient and environmentally friendly production, it is imperative that oxide levels in the fluoride melts are well controlled. Proper control of oxide levels in the fluoride melt can, however, be assumed as a challenge for the rare earth metal industry due to the current lack of state of the art technology as compared to more traditional electrowinning industries like the Al metal industry.

The use of modified linear sweep voltammetry to determine the oxide (aluminium oxide) concentrations in fluoride (Na_3AlF_6) melts is very common for the primary Al production industry [3-7]. However, literature search by the authors of the present paper indicate that no such studies have been reported for the rare earth metal production industry. The voltammetry measurements make use of a phenomenon called anode effect that occurs when the oxide concentrations in fluoride melts get depleted during electrolysis such that the perfluorocarbon gases formed cover the anode surface resulting in peaking of the voltage and reduction in the current [6, 8]. The measurements involve applying a rapid voltage sweep to an electrode assembly consisting of a graphite anode and a cathode in a fluoride melt by means of a voltage-controlled source of electric power connected to the electrodes. By monitoring the current passing through the electrode assembly during each sweep, the voltage and current at which anode effect is induced is recorded [4]. The voltage at which the anode effect occurs is observed to vary with the concentration of oxides in the electrolyte [4, 6, 7]. Haverkamp et. al. [6], observed that the potential at which anode effect occurs increases with increasing oxide concentration. It is thus, possible to correlate the oxide concentration with the applied potential at anode effect within a defined range of parameters. This makes the voltammetry technique suitable for determining oxide concentration in fluoride melts when appropriate calibrations are done [4]. This paper reports on a study of the dissolution of rare earth metal oxides in their corresponding fluoride melts during electrowinning. The aim of the study is to attempt to provide an online means of controlling the oxide concentration during electrolysis in the rare earth metal industry. This involves incorporating fast voltage sweep voltammetry using a critical current density (CCD) probe as a technique for online measurement of the rare earth metal oxide concentration during electrolysis. The solubility of the oxides of Pr, Nd as well as their mixtures in their corresponding fluoride melts at different times during electrolysis was also investigated.

Experimental

The experiments involved the addition of the rare earth metal oxides into their respective fluoride melts that had been heated up to ca. 1040 °C. The additions are done every 30 minutes and continuous measurement of the electrochemical response such as voltage and current are also taken. Sampling of the electrolyte was done during the additions and these samples were later analysed by LECO. XRD analysis was also done when needed to investigate the phases present. The duration for the experiments varied between 3 to 6.5 hours. The concentration of the electrolyte was kept at 50 mol% rare earth metal fluoride (or mixture) and 50 mol% LiF for all the tests, while the working temperature was kept approximately at 1040 °C. The chemicals used for the tests are NdF_3 (Industrial grade), PrF_3 (Jiayuan Advanced Materials, 99.9 %), LiF (Sigma-Aldrich, 99 %), Nd_2O_3 (Alfa Aesar, 99.9 %), Pr_6O_{11} (Alfa Aesar, 99.9 %), $\text{Nd}_2\text{O}_3\text{-Pr}_6\text{O}_{11}$ (Industrial grade) and Pr_2O_3 (Alfa Aesar, 99.9 %). All the chemicals were prior to the experiments kept under dry conditions and preheated to ca.

120 °C before use. The experimental setup consisted of a pure graphite crucible with an internal diameter of ca. 77 mm filled with electrolyte (approx. 1 kg) placed in a steel furnace together with a thermocouple type S as well as a CCD graphite probe and a graphite stirrer as shown in Figure 1. The stirrer as well as the CCD probe were rotated at 80 rpm and 100 rpm, respectively. The CCD probe was rotated to avoid the situation of oxide concentrating around the tip. The CCD graphite probe acted as the working electrode while the graphite crucible was the counter electrode for all the measurements. The whole assembly was placed in a resistance heating furnace that was purged by argon gas and water cooled. Electrochemical measurements were carried out by means of a computer controlled voltage source (HP 6032A system power supply) connected to the electrodes (anode and cathode) assembly and IP sensors (Alumina sensor model 003D). Fast voltage sweeps of 100 V/s were applied to the CCD graphite probe by means of the computer controlled voltage supply and the current response was monitored and recorded.

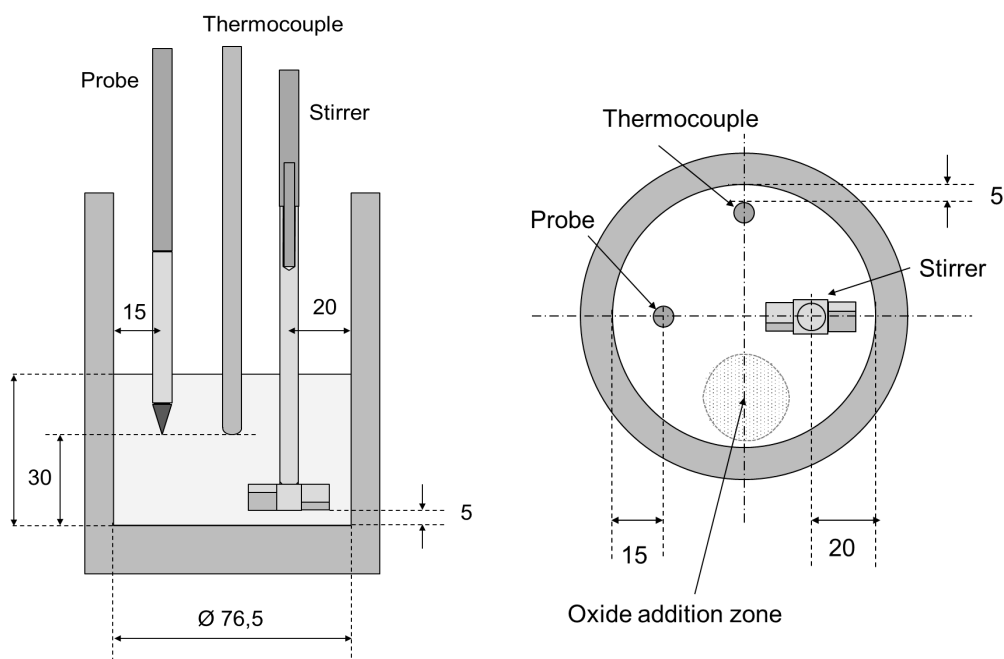


Figure 1. Experimental Setup showing some important parts.

Results and Discussions

Results from the studies showed that the rare earth metal oxides dissolved in rare earth fluoride melts behave in the same way as alumina dissolved in cryolitic melts where the potential at which anode effect occurs depends on the oxide concentration [4]. It was observed that the anode effect occurs at lower potentials for lower oxide concentrations while it occurs at higher potentials as the oxide concentration increases. Figure 2 shows the data from an experiment involving the dissolution of Nd_2O_3 in a 50-50 mol% LiF-NdF_3 electrolyte. The oxide concentration was increased over the period of the experiment. Thus, the oxide concentration at

time 0 minutes was the lowest whereas the maximum concentration was at time 360 minutes.

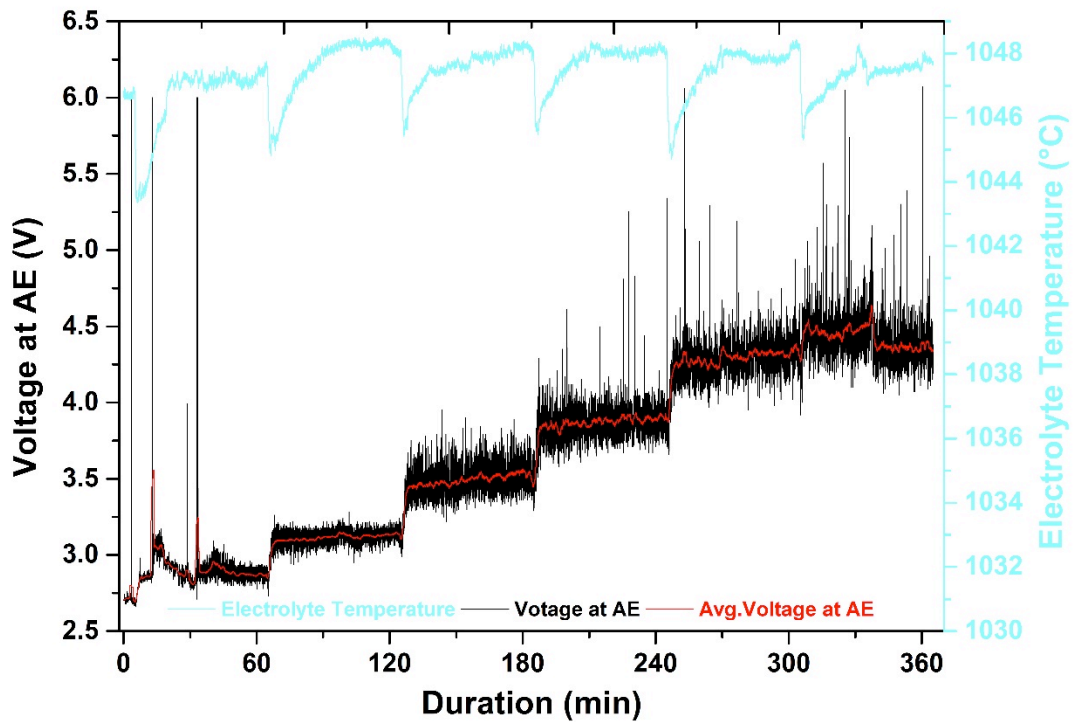


Figure 2. Evolution of the voltage at anode effect with time.

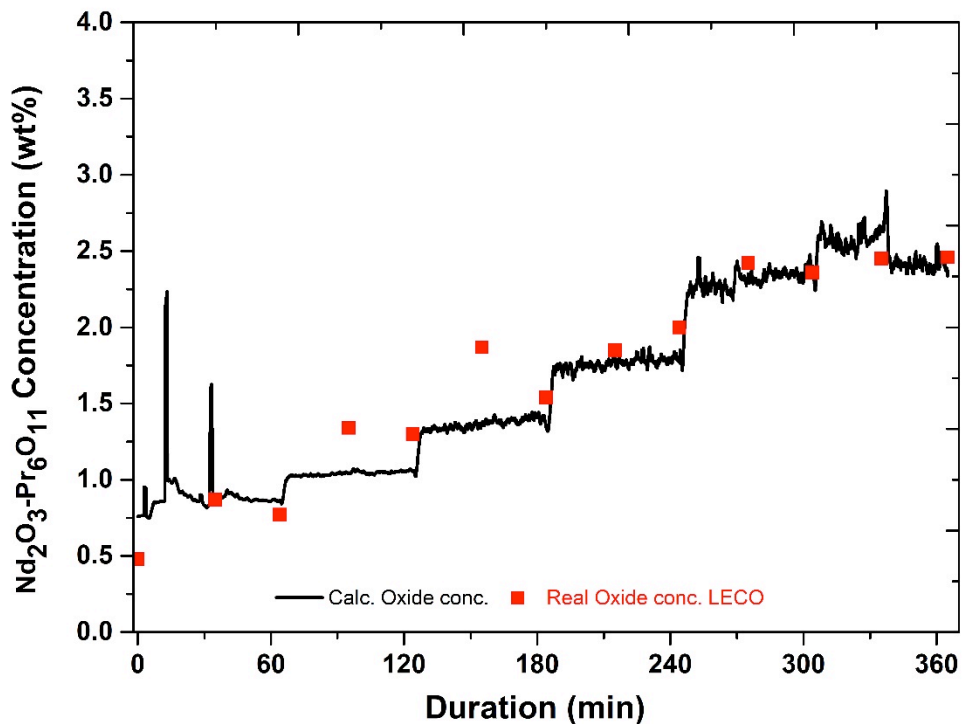


Figure 3. Calculated and real oxide concentration from LECO analysis

The dependence of the potential at which anode effect occurs on the oxide concentrations provided an opportunity to approximate the oxide concentrations as discussed by Haverkamp et. al. [4]. For the experiments discussed in the present paper, the approximate oxide concentrations were calculated using the potential at anode effect. To further prove the concept of approximating the oxide concentration using the potentials, melt samples were taken during the probe measurements and analysed using LECO analysis to determine the actual oxide concentrations. Figure 2 displays a curve showing the calculated oxide concentration and the LECO analysis results of the actual oxide amounts in the electrolyte. It can be seen from the figure that the approximated value agrees very well with the LECO data. This implies that with very good calibrations, the method can be applied as an online method for monitoring the oxide concentration.

Acknowledgement.

Financial support from the European Union's Horizon 2020 and Innovation Programme under Grant Agreement No. 776559 is very much appreciated.

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