

Influence of the electrolyte composition on the molten salt electrolysis of didymium

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Acknowledgements:

This work was supported by the FP-7 EU Program Grant No. 309373 “Development of a Sustainable Exploitation Scheme for Europe’s rare earth Deposits” (EURARE).

Abstract

Separation of neodymium (Nd) and praseodymium (Pr) by solvent extraction is difficult and costly process due to their similar physical properties. Knowing that praseodymium even improves some magnetic properties of Nd-based magnets¹⁻³ skipping this step and employing directly molten salt electrolysis of their mixed oxides (didymium) is meaningful.

Due to Chinese monopoly in rare earth metal production, scientists are confronted with the lack of scientific articles and difficult access. Some known papers^{4, 5} in English report only viability of the process but without further explanations and are outdated, whereas accessible Chinese do not offer enough data⁶⁻⁸.

Cell setups and process parameters for neodymium production such as electrolyte electrochemical and physical properties⁹⁻¹¹, neodymium oxide solubility^{12, 13}, current densities¹⁵ and off-gas evolution¹⁴ are nowadays more-less known. Although neodymium and praseodymium have similar physical properties addition of praseodymium impact all mentioned parameters.

In this study, as the first step toward feasible didymium electrolysis is investigated influence of electrolyte on the metal composition. Neodymium electrolysis is usually done in NdF₃-LiF electrolyte but didymium presumably requires electrolyte modifications. The electrolysis of neodymium and praseodymium (didymium) mixed oxide with a ratio of 66:34 wt% is done in different electrolytes at 1100 °C and the final metal composition is determined by XRF and ICP analytical methods. The ratio of the oxides used is based on the solvent extraction results from the Kvanefjeld REE

deposit containing mineral steenstrupine^{16, 17} obtained during the EURARE project¹⁸. Chronoamperometry of all electrolytes without and with 1 wt% of didymium oxide is conducted where process potential window is established. Simultaneously are those measurements followed by an in-situ off gas FTIR-spectrometer where the evolution of CO, CO₂, CF₄ and C₂F₆ gasses and anode effect could be spotted. Electrolyses with anodic current density 0,46 A/cm² and cathodic 4,5 A/cm² ran for couple of hours with a dosage of 1 wt% of didymium oxide as soon as greenhouse gasses are detected and obtained metal was analysed by X-ray fluorescence spectroscopy (XRF) and Inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Results indicate that the electrolyte composition has insignificant influence on the critical potential/current process window but the amount of the dissolved oxides does. Pr-oxide is more soluble in its own fluoride salt and it led to higher praseodymium amount in metal obtained from electrolyte with high praseodymium-fluoride content as can be seen in Table 1. Furthermore, theoretical concentration activities of Nd and Pr are almost exactly transferred to composition. During and after trials corrosion of crucible and anode are noticed and are related to spontaneous reduction reaction of mixed Pr-oxide to Pr₂O₃. Next step of this work will be the long-term electrolysis in order to determine the stationary Nd/Pr ratio.

Table 1: Compositions of starting electrolyte and metal content in obtained alloys determined by XRF analysis

Electrolyte composition, wt%	Nd, wt%	Pr, wt%
NdF ₃ -LiF (87,5 - 12,5)	95,8	2,3
NdF ₃ -PrF ₃ -LiF (78,75 - 8,75 - 12,5)	85,7	13,9
NdF ₃ -PrF ₃ -LiF (57,75 - 29,75 - 12,5)	70,4	29,0

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