

Novel Reactive Anode for Electrochemical Extraction of Rare Earth Metals from Rare Earth Oxides

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Abstract Electrolytic production of metallic neodymium is carried out in fused fluoride salts containing neodymium oxide. Two major challenges pertaining to neodymium production are (a) low oxide solubility, (b) possibility of anodic fluorine gas evolution if the electrolysis rate exceeds feeding rate of neodymium oxide. In this study, a novel method is proposed in which iron fluoride (FeF_3) is used as a fluorinating agent to convert neodymium oxide into neodymium fluoride. Electron Probe Micro Analysis (EPMA) results of as-converted salt show a complete conversion of neodymium oxide into neodymium fluoride. In the electrolysis process, iron is used as a reactive anode with electrochemical dissolution of iron into the melt, thus preventing fluorine gas evolution at the anode. Therefore, the fluorinating agent is constantly regenerated in situ which enables the continuous conversion of neodymium oxide feed. The cathodic product is a Nd–Fe alloy which can be directly used as a master alloy for the production of NdFeB permanent magnets.

Keywords Rare earth · Electrochemical extraction · Reactive anode

Introduction

The dominant industrial method for the extraction of rare earth metals from their oxides is the molten salt electrolysis process [1–3]. In comparison to hydrometallurgical processes, lower energy consumption, higher efficiency and higher purity of the deposits are advantages in molten salt routes compared to hydrometallurgy processes [4–6]. Solubility of the rare earth oxide (REO) in the fluoride electrolyte is an important factor, since it is the dissolved oxide that is subjected to electrolysis.

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However, the solubility of rare earth oxide in molten alkali fluoride does not exceed 4 wt% [7–9]. Moreover, neodymium oxide forms likely neodymium oxyfluoride in molten fluoride salts. Oxyfluoride formation has been reported to affect the neodymium electrodeposition adversely [10]. Another challenge in neodymium production is fluorine gas evolution on the carbon anode when the electrolysis rate exceeds the rare earth oxide feeding and dissolution rate [11].

Herein we adopt a two-fold approach to address the solubility issue of neodymium oxides in the fluoride melts. Initially, REOs are treated with strong fluorinating agents like FeF_3 which converts REOs to REF_3 . To overcome halogen evolution on the anode, a reactive anode was employed. Iron was anodically dissolved re-generating the fluorinating agent FeF_3 in situ in the electrochemical reactor. The rare earth fluoride thus formed can subsequently be processed through the electrolysis route in the same reactor to extract rare earth metal as the cathodic deposit. In this concept, the REO dissolution in the molten fluorides would become redundant due to the rapid and complete conversion of the oxide into the fluoride as REF_3 .

Experimental

Lithium fluoride (98.5%-Alfa Aesar) was mixed with neodymium oxide (Rhodia) in a glove box. In the experiments for the conversion of neodymium oxide to neodymium fluoride, iron fluoride (97%-Alfa Aesar) was added to the mixture and the mixture was charged into a graphite crucible. For these experiments, the stoichiometry equivalent concentration of fluorinating agent was used in order to reach the complete conversion of Nd_2O_3 into NdF_3 . A molybdenum rod (2 mm diameter) was used as cathode. The immersion depth of the Mo rod was measured after each experiment. An iron rod (98%-Salomon metals, 2 mm diameter) was used as anode. All experiments were performed at 950 °C under a purified argon atmosphere. The argon gas was purified by passing through KOH flakes in order to remove traces of CO_2 sulphur and also through silica gel and P_2O_5 to remove moisture. The gas was passed through a tube furnace containing Ti sponge which was held at 1123 K (850 °C) in order to remove the trace amount of O_2 . The samples were removed from the furnace and immediately quenched in liquid nitrogen after the experiment.

The samples were analyzed by Electron Probe Micro Analysis (EPMA), in order to derive the phases that are formed during the experiments from the local compositions. WDS point analyses or mappings were performed at 15 kV–15 nA and for the quantification, standard samples were used.

Results and Discussion

EPMA mapping of the sample from the $\text{LiF-Nd}_2\text{O}_3\text{-FeF}_3$ salt bath that was quenched in liquid nitrogen after 3 h at 950 °C, is shown in Fig. 1. It can be seen that neodymium and oxygen do not occur in the same regions, whereas iron and oxygen

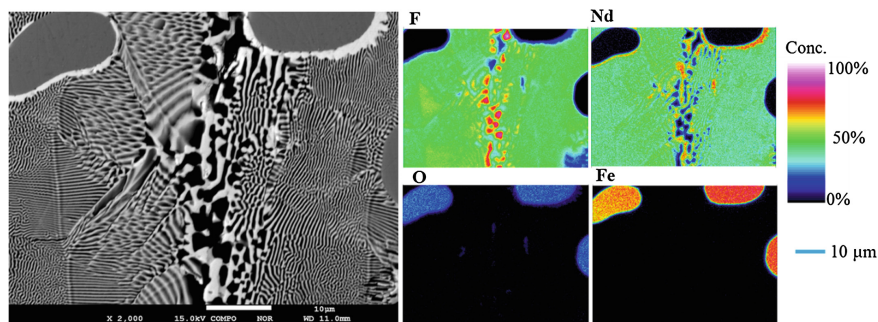


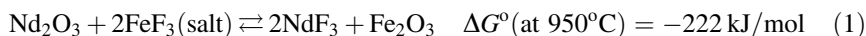
Fig. 1 EPMA mapping of LiF-Nd₂O₃-FeF₃ sample after fluorination treatment showing the presence of NdF₃ and FeO. Note that Li cannot be detected in these EPMA measurements

Table 1 EPMA quantification results of LiF-Nd₂O₃-FeF₃ sample (in at.%) after fluorination treatment showing the presence of NdF₃ and FeO_x

Element	NdF ₃	FeO _x
F	72	–
O	–	54
Nd	26	–
Fe	–	45

are clearly distributed in the same area, confirming the iron oxide formation. Neodymium has a high concentration around the FeO boundaries. The light-grey lamellar phase is NdF₃ within the dark LiF, indicating LiF-NdF₃ eutectic microstructure. In the EPMA mapping, in which Li cannot be detected, complete conversion of neodymium oxide to neodymium fluoride is exhibited.

The EPMA quantitative results are presented in Table 1. The composition in the column NdF₃ was measured in the Nd-regions of Fig. 1 and the FeO_x composition in the Fe- and O-rich regions. In this table, the presence of NdF₃ (26 at.% Nd and 72 at.% F) and FeO_x (45 at.% Fe and 54 at.% O) are confirmed. The phase indicated as iron oxide can be a mixture of FeO and Fe₂O₃, since the concentrations can be related to magnetite phase (Fe₃O₄). Based on the calculated standard Gibbs energy (FactSage 7.0) for the reaction (1),



conversion of neodymium oxide to neodymium fluoride using iron fluoride is feasible. According to this reaction, Fe₂O₃ formation is expected, but as EPMA results show, the oxide of iron which is formed can be wüstite or non-stoichiometric FeO_x. In the argon ambient and low oxygen pressure atmosphere, hematite (Fe₂O₃) will not be formed or depending upon the oxygen pressure prevailing, the formed Fe₂O₃ is decomposed to Fe₃O₄ and FeO. At high temperatures (more than ca. 560 °C), stable oxide is wüstite (FeO).

NdF_3 , formed as the result of the reaction between Nd_2O_3 and FeF_3 , will go through the electrolysis process. In this process, the cathodic reaction would be:



Whereas in the anodic part of the reaction, fluorine gas is generated if an inert anode such as graphite is used:



In order to avoid fluorine gas formation on the anode, the novel idea in the present work is to use iron as reactive anode. In this process, iron in the anode is dissolved in the salt as the result of an anodic reaction which leads to in situ formation of iron fluoride. Besides avoiding the fluorine gas evolution, another advantage of this method is that iron fluoride is generated and used in the system, which leads to less material consumption, meaning that fluorinating agent is constantly generated and consumed in the system. In this case the anodic reaction will be iron dissolution:



A series of experiments was carried out in order to examine the electrochemical dissolution of iron in the molten salt. In these experiments iron served as anode and Mo as cathode, which were immersed in $\text{LiF-Nd}_2\text{O}_3$ mixture. The experiment was performed in constant current mode at 1.5 A for 3 h at 950 °C. Based on Faraday's law, considering 3 exchanged electrons in the cathodic reduction of neodymium metal, mass of the dissolved iron can be calculated:

$$m = ItM/nF \quad (5)$$

where I is the electrolysis current in A, t is the time of the electrolysis in s, n is the number of exchanged electrons, F is the Faraday's constant ($F = 96,500 \text{ }^\circ\text{C}$), m is the mass of the element in gram and M is the atomic mass of the element.

The cathodic product on the molybdenum electrode was analysed by EPMA. The result is shown in Fig. 2.

From EPMA analysis result, it can be seen that a layer of iron is formed on the molybdenum cathode and neodymium is reduced onto this layer. Fe might be deposited from the iron fluoride, which is formed from dissolution of the iron anode, since iron fluoride has a less positive decomposition voltage compared to neodymium fluoride. Part of the iron fluoride which reacts with neodymium oxide based on reaction (1), forms iron oxide. The dissolved iron oxide can also participate in the electro-decomposition process, and co-deposition of Fe occurs at the cathode. Nd-Fe alloy production is desirable since it can be used as master alloy for magnet production. The challenge would be as to how to remove the undissolved iron oxide in order to minimize their side effect on cathodic deposition of Nd.

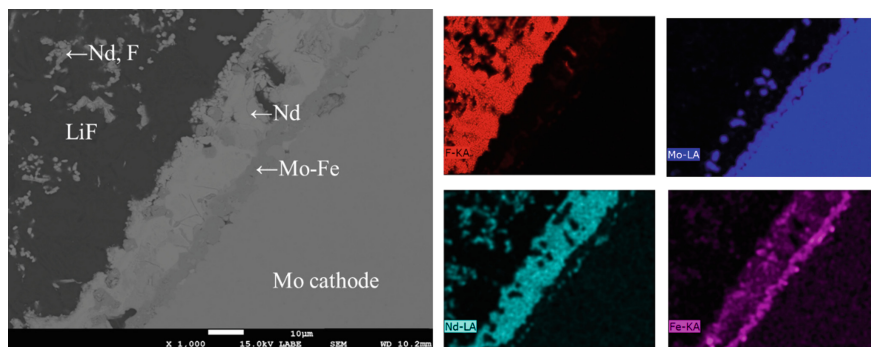


Fig. 2 EPMA mapping of the deposited product on the molybdenum cathode after 3 h electrolysis at 950 °C, using iron as anode

A new design of a two-chamber furnace system is one way for removing the undissolved oxide, which is presently under study. A possible alternative may be to take advantage of the density difference between the formed oxide and the fluoride bath in order to separate the oxides from the molten salt.

Conclusion

The problem of low solubility of the neodymium oxide in molten fluorides is solved to a large extent by converting neodymium oxide to neodymium fluoride in situ. Once neodymium fluoride is formed, it can subsequently be electrolyzed and extracted on the cathode. In this study, a novel method is studied in which iron is used as anode, promoting electrochemical dissolution of iron into the melt, thus preventing fluorine gas evolution at the anode. Therefore, the fluorinating agent is constantly regenerated in situ which enables the continuous conversion of neodymium oxide feed. The cathodic product is Nd–Fe alloy which can be directly used as a master alloy for the production of NdFeB magnets.

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