

Stabilisation of Neodymium and Praseodymium molten salt electrolysis to avoid unwanted side reactions

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Abstract

With the increasing attention paid to the climate, the pressure on the industry to develop and promote alternative drives is also increasing. One alternative to the conventional petrol engine is the use of electric engines. Just like electric generators, for example in wind turbines, these require very strong magnets to achieve the highest possible efficiency. Currently, Neodymium-Iron-Boron magnets are used for this purpose. The Neodymium in those magnets is partly substituted by Praseodymium. Since Nd and Pr occur in the ore together as didymium one more process step would be necessary to purify neodymium. By using the alloy of both elements this additional process step can be eliminated to save costs.

Molten salt electrolysis is applied in the production of the alloy. In this process neodymium and praseodymium in their oxidic forms are charged into fused salt, the electrolyte, which consists of neodymium fluoride, praseodymium fluoride and lithium fluoride. The oxide dissolves and migrates in an oxyfluoride form, as expected, towards the electrodes. At the graphite anode oxide anions are formed to CO/CO₂ while at the molybdenum cathode the Nd and Pr cations are reduced and the liquid alloy is deposited in another molybdenum crucible.

In order to develop a long-term stable electrolysis process, various experiments have been carried out. Important for the process is the stable composition of the electrolyte. In the present study, the electrolyte consists of 65.7% NdF₃, 21.8% PrF₃ and 12.5% LiF at the beginning of each trial. This composition is chosen to obtain a high electrical conductivity and to keep the melting point of the electrolyte at a minimum. Experiments have shown that after about eight hours of electrolysis the anode effect occurs more often if only oxides are fed to the system. One reason for this unstable condition seems to be an insufficient solubility of the oxides. Samples of the electrolyte which were analysed by the EPMA confirm this assumption. While the oxide was still finely distributed at the beginning of the experiment, it formed large lumps towards the end of the experiment.

This behaviour is related to the lithium fluoride content in the electrolyte which lowers the melting temperature and increases the electrical conductivity. Lithium fluoride is also a donor for F⁻ ions which are required for the above-mentioned oxyfluorides. Therefore, lithium fluoride is important for the dissolution/solubility behaviour of the oxides. In the present study, several electrochemical measurements were conducted to examine the complex system. It was possible to reactivate an already used electrolyte by feeding different amounts of lithium fluoride. While doing this the maximum reached current density as well as the maximum reached potential before the anode effect could be raised significantly.

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