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E - Electrochemistry

ELECTROCHEMICAL DEPOSITION OF NEODYMIUM AND PRASEODYMIUM ON MOLYBDENUM FROM MOLTEN FLUORIDE

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ABSTRACT

Neodymium and praseodymium were electrochemically co-deposited onto Mo cathode applying constant potential, from fluoride-based molten salts containing the corresponding rare earth oxides. According to the recorded voltammograms, it appears that in the investigated system, the electrodeposition of neodymium proceeds as a two-step reduction process: Nd(III)→Nd(II) and Nd(II)→Nd(0), whilst the praseodymium deposition proceeds as an one-step reduction process: Pr(III)→Pr(0). However, it was also recognized that at the same time a substantial amount of NdF_2 was formed as a result of the disproportionation reaction between the electrodeposited Nd metal and Nd(III) present in the electrolyte.

The deposit on the working electrode surface was recorded by optical microscopy and analyzed by X-ray diffraction (XRD). The analysis made upon the applying the potentiostatic deposition regimehas shown Nd/Pr metals present on the molybdenum cathode.

INTRODUCTION

Recycling in the context of the circular economy is becoming increasingly important, including the field of neodymium iron boron magnets, which are used in applications such as computer hard drives, hybrid and electric vehicles (HEVs/EVs) and wind turbines [1]. Neodymium and praseodymium rare earth elements are components of NdFeB magnets. There are various approaches to the recovery of rare earth elements (REEs) from the end-of-live magnets, such as hydrometallurgical and pyrometallurgical processes, liquid metal extraction, molten salt electrolysis [2]. An effective recycling process of these magnets could make rare earth mining and subsequent process steps up to the metal partially obsolete [3]. One recycling route for magnets is, firstly, to oxidise magnet powder. The next step is to melt these oxides which separates the ingredients into an iron rich metal phase and a REE rich slag. In the last step of this route, the rare earth elements, namely neodymium, praseodymium and dysprosium, can be won in the molten salt electrolysis.

Therefore, in this work, the deposition behaviour of neodymium and praseodymium from the fluoride molten salts system was investigated. More specifically, the reaction mechanism of neodymium and praseodymium deposition was studied in the fluoride based molten salts containing the rare earth oxides, in order to provide the appropriate potential for increase of Nd and Pr metal deposited on the cathode surface. Using a molten fluoride salts electrolyte instead of chloride ones is expected to provide advantages like higher current efficiencies, lower hygroscopicity and higher conductivity. However, there is a number of challenges remaining connected to the composition of the electrolyte based on neodymium, praseodymium, lithium fluoride and neodymium and praseodymium oxides and their influence on all aspects of desired effective metals deposition.

EXPERIMENTAL

The electrochemical experiments were conducted in a steel cell described elsewhere [4,5], with a three-electrode system: a working electrode (WE) molybdenum (Mo, 2 mm diameter, EWG 99.95%), a counter electrode (CE) high purity glassy carbon (GC, 4 mm diameter, >99.99% HTW SIGRADUR® G) and a reference electrode (RE) tungsten (W, 1 mm diameter, EWG 99.95%). The chemicals used for the experiments and the composition of the electrolyte used are shown in Table 1.

Table 1. Composition of the electrolyte

Component	Supplier	Purity	Weight percentage [wt.-%]	Molar ratio [mol.-%]
NdF_3	Treibacher, Althofen, Austria	≥99.9%	63.17	35.26
PrF_3		≥99.9%	20.96	11.90
LiF		≥99.5%	12.02	51.99
Nd_2O_3		≥99.9%	1.92	0.64
Pr_6O_{11}		≥99.9%	1.92	0.21

To prepare the electrolyte, the fluorides have been dried in a furnace for 24 h at 523 K. They were then were manually mixed and molten in a high purity graphite crucible to homogenise the melt. This process is conducted in a vacuum induction furnace at up to 1373 K which is able to operate at overpressure to counteract the high vapour pressure of the fluorides, under 1800 mbar of argon. The oxides were also dried in a furnace for 24 h at about 393 K before they have been added to the electrolyte.

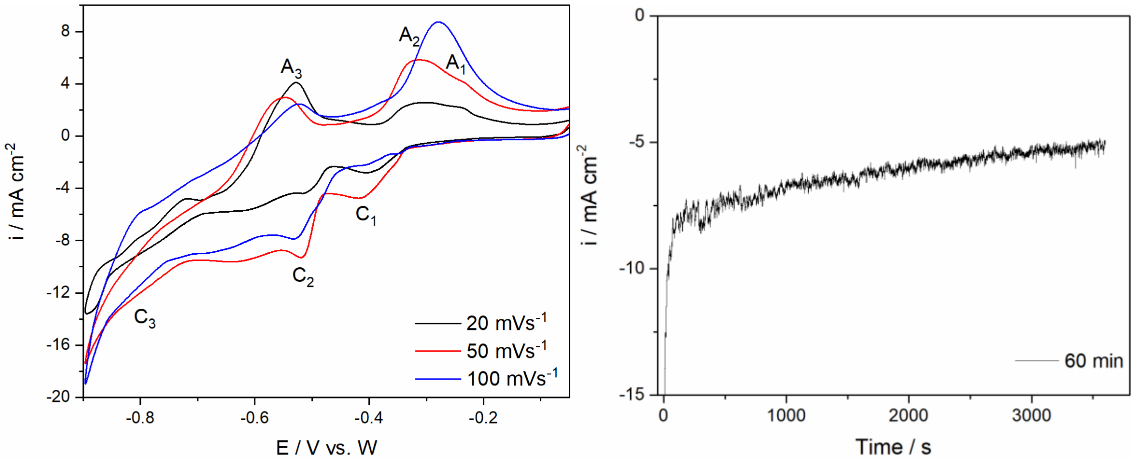
The electrochemical measurements have been conducted at a process temperature of 1323 K, controlled by a thermocouple type B, and under a continuous flow of argon to prevent oxidation. An IviumStat potentiostat (5 A/10 V; Ivium Technologies) was used for electrochemical measurement: cyclic voltammetry (CV using various scan rates in 50-300 mV/s range) and chronopotentiometry (deposition experiments were carried out for up to 240 min at different constant overpotentials).

The surface of the working electrode obtained after deposition was examined by an optical microscope (Keyence; model VH-Z100R, Japan). The deposits and the remaining electrolyte on the electrode were analysed by X-ray diffraction (XRD) with Philips PW 1050 powder diffractometer at room temperature with Ni filtered CuKα radiation (λ= 1.54178 Å), scintillation detector within 20–85° 2θ range in steps of 0.05 and scanning time of 5 s per step.

RESULTS AND DISCUSSION

An example of the cyclic voltammograms recorded on the Mo working electrode in the fluoride-based molten salts containing rare earth oxide Nd_2O_3 and Pr_6O_{11} are shown in Figure 1.

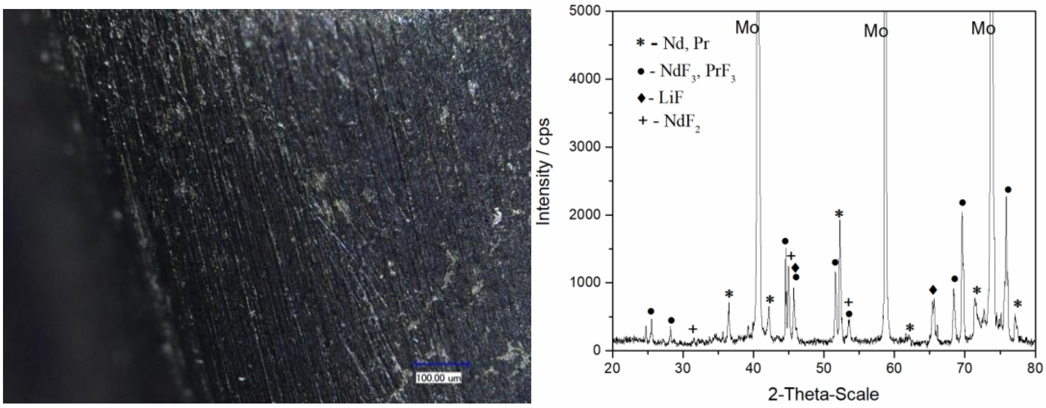
In the electrolyte with Nd_2O_3 and Pr_6O_{11}, the anodic and cathodic current peaks are not very clearly defined. In the presence of Nd_2O_3 and Pr_6O_{11}, there are three cathodic (C_1, C_2, C_3) and three anodic (A_1, A_2, A_3) current waves to be recognized. The peak C_1 at ≈ - 400 mV vs. W should reflect the reduction of Nd(III) to Nd(II), the cathodic peak C_2 at ≈ - 550 mV vs. W should record the further reduction of Nd ions to the metal, namely Nd(II) to Nd(0). At further negative applied potential around - 800 mV vs. W, the third cathodic peak C_3 is most probably a reflection of the reduction of Pr(III) to Pr(0) metal. The anodic current waves (A_3 at ≈ - 600 mV vs. W, A_2 ≈ - 350 mV vs. W and A_1 ≈ - 200 mV vs. W) should reflect the reverse processes to those presented by C_1, C_2 and C_3, in other words, dissolution of the deposited praseodymium to Pr(III) (A_3 peak) and neodymium to Nd(III), (A_2 and A_1 peaks). In addition, only when the slow scan rates were used (20 and 50 mVs^{-1}), the anodic current wave A_1, which corresponds to oxidation of Nd(II)→ Nd(0), could be detected.



a) b)

Figure 1. a) CV recorded on Mo working electrode in molten NdF_3+PrF_3+LiF+Nd_2O_3+Pr_6O_{11} electrolyte, with different scan rates; b) potentiostatic deposition on Mo from the same electrolyte for 60 min at constant potential of - 900 mV vs. W; T=1323 K.

The appearance of the Mo cathode surface under an optical microscope after constant potential deposition at - 900 mV vs. W for 1 h from the used electrolyte is presented in Figure 2.a).



a) b)

Figure 2. a) Optical image of the surface of the Mo cathode after deposition from molten NdF_3+PrF_3+LiF+Nd_2O_3+Pr_6O_{11} electrolyte, at - 900 mV vs. W for 3600 s, at 1323 K (the solidified electrolyte was removed from the electrode); b) XRD pattern of the Mo working electrode from Figure 1.a).

To ensure that Li will not be present in the deposit, the deposition was performed at - 900 mV vs. W, which was a potential only ≈ 100 mV more negative than the peak potential value of the cathodic peak C_3. The chosen potential was cathodic enough to sustain Nd and Pr metal deposition, with a deposition current density of ≈ - 6 $mAcm^{-2}$, Figure 1.b). There is obvious evidence of the deposit other than the solidified electrolyte which has been removed before the photo was taken. The XRD pattern of the same working electrode and the deposit thereon is given in Figure 2.b). The diffractogram revealed the presence of Nd and Pr metal in substantial quantity and verified that the proper potential was applied for deposition. Unfortunately, in the diffractograms recorded, it is difficult to distinguish between the possible peaks belonging only to Nd and only to Pr, because of the high similarity of their crystal lattices. Nd and Pr metal both have hexagonal crystal lattice and very similar lattice parameters. Therefore, although the peaks are characteristic of either of the two metals, we had to attribute to both of them, Nd and Pr [JCPDS No. 03-065-3424 for Nd, and JCPDS No. 01-089-2921 for Pr]. Well defined peaks reflecting the presence of Nd/Pr metal on the working electrode surface could be recognized by the following 2Θ values: 36.40°/36.27°; 41.83°/41.89°; 52.3°/52.14°; 62.05°/62.16°, 71.75°/71.45°, 77.33°/77.01°. However, the presence of the melt residue (NdF_2, NdF_3, PrF_3, LiF) could not be avoided. Evidence of NdF_2, which was formed during the potentiostatic deposition process due to the disproportionation reactions between Nd metal deposited and Nd(III) ions present in the electrolyte, was rather well pronounced [4,5].

CONCLUSION

Neodymium and praseodymium were successfully electrodeposited on Mo cathode by applying constant potential from fluoride-based Nd, Pr and Li molten salts containing rare earth oxides (Nd_2O_3 and Pr_6O_{11}). It seems that in the investigated systems, the reduction of Nd(III) ions to the metal proceeds as a two-step reduction process: Nd(III)→Nd(II) and Nd(II)→Nd(0), whilst the reduction of Pr(III) ions to the metal is a one-step reduction process: Pr(III)→Pr(0), It appears, also, that these reactions under the applied conditions are reversible and transport- controlled because the electrolyte was not stirred. The results recorded by the electrochemical techniques applied on the system used suggested that Nd and Pr metal can be electrochemically deposited on Mo electrode, and the XRD analysis confirmed the assumption.

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