NEODYMIUM ELECTRODEPOSITION STUDY
OVER PT ELECTRODE IN FUSED EQUIMOLAR NA CL-KCL
MIXTURE AT 700 °C

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ABSTRACT

The electrochemical route to obtain neodymium and neodymium alloys from molten salts electrolytes is very important as an initial step to produce permanent magnets like Nd-Fe-B. This study is based on the electrochemical investigation on a Pt electrode, of neodymium electrolysis from NaCl-KCl equimolar mixture with prepared anhydrous NdCl₃ at 700 °C using cyclic voltammetry technique. Non soluble compounds were formed between electrodeposited Nd and Pt electrode. Additional results on a Mo electrode revealed a one step three electrons reduction process.

INTRODUCTION

The rare earth metals show technological applicability mainly in the corrosion resistant alloy preparations and recently in special magnets like Sm-Co and Nd-Fe-B (1). The rare earth elements naturally occur within three principal minerals: the bastnasite, the monazite and the xenotime (2). Pure rare earth element preparation is quite difficult as a result of its very similar chemical and electrochemical properties (3). The usual chemical routes through rare-earth separation as salts or oxides are ion exchange and solvent extraction. These compounds can be used as the precursor to obtain rare earth metals either by metallothermic or electrometallurgical reduction.

The electrometallurgical route has some advantages compared with the metallothermic (4) for instance: metal preparation in only one step, the electrode reaction is fast, the rare earth metals reactivity can be reduced by the codeposition to form alloys and the possibility to realize electrochemical kinetics studies. Morrice and Wong (5) published an excellent review of electrolytic production of rare earth metals from both chloride and fluoride electrolytes.

The purpose of the present work is to investigate the Nd³⁺ ion electrochemical behavior on a Pt electrode using a large number of prepared anhydrous NdCl₃ with NaCl-KCl eutectic mixtures. The cyclic voltammetry technique has been used to gain insight for future laboratory scale of pure or neodymium alloys preparation.
EXPERIMENTAL

Voltammetric experiments were carried out in an AISI 304 stainless steel electrochemical cell, (Fig. 1). Platinum (0.5 mm in diameter), Ag/AgCl (6) + NaCl-KCl inside an alumina container and a graphite crucible were the working, reference and auxiliary electrodes, respectively. The temperature for all experiments was fixed at 700 °C.

Cyclic voltammetry was performed using an EG&G potentiostat model 173 with a Universal Programmer model 175 connected with an XY recorder model RE 0074.

Both solvent mixture and solute were treated to eliminate the water and the hydration degree was determined by thermogravimetric analysis.

RESULTS AND DISCUSSION

Platinum electrode

The reduction potential of the neodymium ions on a Pt electrode occurs at -1.25V/E_ref for all three concentrations used (0.25 M, 0.5 M and 1.0 M). This can be seen at the complete and very reproducible voltammogram in (Fig. 2) for 0.5 M NdCl₃. The current peaks A/A' are ascribed to the deposition and dissolution of potassium ions, the current peaks C/C' are attributed to deposition and dissolution of Nd³⁺ ions and the current peaks E and D can be better understood after increasing the concentration of the Nd³⁺ ions in the chloride melt.

Changing the concentration of the Nd³⁺ ions between 0.25 M, 0.5 M and 1.0 M and restraining the cathodic potential at -2.1 V/E_ref the current peaks C/C' increase as expected (Fig. 3). For all concentrations used, a current peak denoted by i appears before the Nd³⁺ ions reduction current peak. At 0.5 M and 1.0 M Nd³⁺ ion concentrations a current peak denoted by ii appears just after the neodymium deposition.

The reduction current peaks i and ii produce corresponding anodic current peaks D and E respectively as a result of the interactions between the metallic neodymium and Pt electrode.

No previous results have been reported for rare earth electrodeposition on Pt electrodes. The electrochemical investigations of rare earth ion reduction on nickel, cobalt and iron electrodes (8,9,10,11,12,13) however, has confirmed a reasonable interaction with deposited species and electrode material revealing the presence of several distinct compounds. Comparing ours results obtained on Pt electrode with...
those in the literature, the voltammograms profile are quite similar besides an existing interaction between the reduced sodium ions from electrolyte and the Pt electrode. The anodic current peaks D and E appearing frequently however, during some experiments, these current peaks show smaller intensities. The phase diagram (14) of Nd-Pt system in (Fig. 4) shows the existing possible compounds.

The voltammogram in (Fig. 5) for 1.0 M NdCl₃ at 750 °C and 800 °C is very reproducible. The anodic peaks D and F increase with the temperature but the corresponding cathodic current peaks are not present indicating that they are surface insoluble products with irreversible reaction mechanism for peak F. The insoluble products formation at platinum surface can be followed comparing the first and second scans from the voltammograms in (Fig. 6). For the first scan the platinum electrode was freshly polished and at the second just after the first one using 1.0 M NdCl₃ at 700 °C. The cathodic/anodic peaks C/C' due to the pair Nd/Nd³⁺, appears on both scans while the cathodic peaks i/i and anodic peaks D/E but not very clear the anodic current F appears only at the second scan. This behavior can be explained by interaction between the electroactive species Nd³⁺ and platinum substratum to form intermetallics compounds.

After the cyclic scan toward cathodic potentials (150 times (600 sec) between -2.0 V and 0.5 V), the Pt electrode was SEM examined. The electrode cross-section of the obtained deposit is showed in (Fig. 7 a, b). The insoluble product is only partially oxidized after scans toward anodic potentials confirming the interaction between Nd and Pt electrode. Qualitative analysis to identify the deposit composition has indicated neodymium and iron. The layer has solidified electrolyte crystals and cracks arising from thermal shock produced by bringing the electrode to a colder region outside the interior of electrochemical cell (Fig. 8).

Cyclic voltammetry was again used to identify electrodeposit compositions through different assays:

♦ sample C: the potential was 150 times scanned (600 sec) between -1.8V and -1.0 V, around the Nd/Nd³⁺ deposition/oxidation peak C/C' region,

♦ sample D, the potential was 75 times scanned (300 sec) between -2.2V and 0.5V, in order to analyze all solvent voltammetric region (see Fig. 2).

The SEM photographs of samples C and D are depicted in (Figs. 9 and 10). The qualitative analysis indicated together with neodymium the iron in sample C and iron and nickel in sample D. These contaminants come from the electrochemical cell and the electrode holder, their reduction peaks do not appear at the obtained cyclic voltammograms with any effect over the Nd reduction peak because its lower bath concentrations. X-ray analysis could not be performed in the thinner electrodeposited electrode layer.
Molybdenum electrode

Using a molybdenum electrode the neodymium ion reduction potential at -1.9 V appears very close to that of potassium ions. The current peak identification, however, was possible only above 0.5 M NdCl₃. In (Fig. 11) the obtained cyclic voltammogram for 0.5 M NdCl₃ at 700 °C shows the A/A’ cathodic/anodic current peaks of K/K⁺ pair, the G/G’ cathodic/anodic current peaks of Nd/Nd³⁺ pair, both under reversible control, and an anodic peak O, due to molybdenum electrode oxidation. At cathodic region no insoluble product was formed over the electrode surface.

With the increasing of the scan rate or the temperature, for any solute concentration, the neodymium ion deposition potential shifts towards the cathodic region, mixing its current peak G with that of the potassium ions, whereas the anodic current peak G’ increases (soluble compound). A possible explanation may be that the potassium ions reduction process is favored, competing directly with neodymium ions reduction. The neodymium anodic peak may be under the influence of the potassium deposition process thereby making its cathodic current peak determination difficult.

The suggested mechanism for the Nd³⁺ reduction on a Mo electrode occurs in only one step of three electrons in a reversible pathway (11). The same can be seen in the voltammogram of (Fig. 11), where only the peaks G/G’ (pair Nd/Nd³⁺) and C/C’ (pair K/K⁺) appear.

CONCLUSIONS

- The electrodeposited neodymium does not form compounds with molybdenum electrode.
- The intermetallic compound formed between electrodeposited neodymium and the platinum electrode appears only when the cathodic potential is scanned many times.
- The voltammogram analysis reinforces previous analysis, showing that the reduction mechanism of Nd³⁺ over Mo electrode occurs in only one step of three electrons in a reversible pathway.
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Figure 1. Electrolytic cell view.

Figure 2. Cyclic voltammogram for 0.5 M NdCl₃ reduction in NaCl-KCl, over Pt electrode (0.16 cm²) at 700°C; v = 0.2 V.s⁻¹.
Figure 3. Cyclic voltammogram for 0.25, 0.5 and 1.0 M NdCl₃ reduction in NaCl-KCl, over Pt electrode (0.16 cm²) at 700°C; v = 0.2 V.s⁻¹.

Figure 4. Nd-Pt system phase diagram
Figure 5. Cyclic voltammogram for 1.0 M NdCl₃ reduction in NaCl-KCl, over Pt electrode (0.16 cm²) at 750 and 800°C; v = 0.2 V.s⁻¹.

Figure 6. Cyclic voltammogram for 1.0 M NdCl₃ reduction in NaCl-KCl, over Pt electrode (0.16 cm²) at 700°C; v = 0.2 V.s⁻¹
Figure 7. SEM micrographs of deposits over the Pt surface electrode.

Figure 8. SEM micrography of deposits with cracks and solid electrolyte over the Pt surface electrode.
Figure 9. Sample C. SEM micrograph of deposit with cracks over the Pt wire electrode

Figure 10. Sample D. SEM micrograph of deposit with cracks over the Pt wire electrode
Figure 11. Cyclic voltammogram: 0.5 M NdCl$_3$ reduction in NaCl-KCl, over Mo electrode (0.16 cm$^2$) at 700 °C; v = 0.1 V.s$^{-1}$