**Obtaining of Nd-Co films by electrolysis in a chloride-fluoride melt**

S I Markovich, A V Popova, V V Semushin and S A Kuznetsov

Tananaev Institute of Chemistry of the Federal Research Centre “Kola Science Centre of the Russian Academy of Sciences”, 184209 Apatity, Russia

E-mail: s.markovich@ksc.ru

**Abstract.** The electrodeposition of neodymium on a cobalt substrate in a chloride-fluoride melt NaCl-KCl -10 wt.% NaF-5 wt.% NdF$_3$ was studied. It is shown that during electrolysis, a coating with a crystal size of 2-5 microns is formed. Microanalysis of the coating determined the electrocrystallization of intermetallic compounds Co$_{17}$Nd$_2$ and Co$_3$Nd on a cobalt substrate.

1. **Introduction**

Rare earth metals (REM) are very important for the production of many industrial products such as computers, LCD screens and lasers. Despite extensive research in the development of new processes for recycling waste of rare earth metals, at present, the level of their recycling remains extremely low. This waste is mostly from the production of magnetic materials, in particular the NdFeB alloy used in the production of hard disks.

In this work, we carried out the investigations necessary for the electrochemical method of recycling the NdFeB alloy, which is a secondary source of neodymium. The method allows one to obtain high-purity neodymium at the cathode, since during the recycling of the alloy, electrorefining from impurities is observed. By using a reactive cathode material, the composition of the resulting intermetallic compounds can be precisely controlled.

2. **Experimental**

The electrolyte was the NaCl-KCl - 10 wt.% NaF - 5 wt.% NdF$_3$ melt, which was placed in a nickel retort. Neodymium was placed in the bottom of the retort in advance. (At the first stage of the study, neodymium was used to eliminate the influence of Fe and B, rather than an NdFeB alloy). A cobalt plate (K0 brand) served as a cathode, and neodymium served as an anode. The neodymium electrodeposition process was carried out at a temperature of 1023 K. The experiment time was 8 hours, the cathodic current density was 5 mA cm$^{-2}$. The cathodic deposits were analyzed by X-ray phase analysis, and the qualitative and quantitative composition of local areas of the samples was carried out by X-ray spectral microprobe analysis.

In principle, for the electrodeposition of neodymium, it is possible to use a chloride melt NaCl-KCl-NdCl$_3$. However, in a chloride melt, the electroreduction of neodymium occurs in two stages [1, 2]:

\[
\text{Nd(III)} + e^- \rightarrow \text{Nd(II)} \quad (1) \\
\text{Nd(II)} + 2e^- \rightarrow \text{Nd}^0 \quad (2)
\]

moreover, the recharge stage (1) is complicated by the disproportionation reaction (DPP) [1]:

\[
\text{Nd(II)} \leftrightarrow \text{Nd(III)} + \text{Nd} \quad (3)
\]

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

Published under licence by IOP Publishing Ltd
The presence of the recharge process and the DPP reaction significantly complicates the process of electrodeposition of neodymium. At the same time, in a chloride-fluoride melt, the discharge of neodymium to metal occurs in a one-stage [3]:

\[
\text{Nd(III)} + 3e^- \rightarrow \text{Nd}^0 \quad (4)
\]

therefore, the use of a chloride-fluoride melt is preferred.

3. Results and discussion

The X-ray diffraction pattern of the cobalt substrate before the experiment is shown in figure 1, and after electrodeposition from the melt (NaCl-KCl) - 10 wt.% NaF - 5 wt.% NdF₃ in figure 2.

![Figure 1. X-ray diffraction pattern of the Co sample before the experiment.](image1)

![Figure 2. X-ray diffraction pattern of the Co sample after the experiment.](image2)

A microimage of the coating on a cobalt substrate is shown in figure 3. As can be seen from figure 3, the coating over the sample area is mainly dark in color, and some areas of the coating are light in color and are characterized by a metallic shine. Microanalysis showed that the dark part of the coating
is mainly carbon. This is confirmed not only by the results of microanalysis, but also by the data of XRD analysis (figure 2).

![Microimage of a coating obtained on a cobalt substrate in the NaCl-KCl - 10 wt.% NaF -5 wt.% NdF₃ melt. Temperature: 1023 K. Electrodeposition time: 8 hours. The cathodic current density: 5 mA cm⁻².](image1)

**Figure 3.** Microimage of a coating obtained on a cobalt substrate in the NaCl-KCl - 10 wt.% NaF -5 wt.% NdF₃ melt. Temperature: 1023 K. Electrodeposition time: 8 hours. The cathodic current density: 5 mA cm⁻².

It was found by IR spectroscopy that the source of carbon is an insignificant content of carbonate ions in NdF₃.

Microanalysis of the light areas of the coating showed the presence of an intermetallic compound with a neodymium content of 22-24 wt.%, which suggests the formation of an intermetallic compound of the composition Co₁₇Nd₂.

![Morphology of the coating on the cobalt substrate obtained after the second electrolysis. Areas for microanalysis of the coating after the second electrolysis (1, 2). Melt: (NaCl-KCl) - 10 wt.% NaF - 5 wt.% NdF₃. Temperature: 1023 K. Electrodeposition time: 8 hours. The cathodic current density: 5 mA cm⁻².](image2)

**Figure 4.** Morphology of the coating on the cobalt substrate obtained after the second electrolysis. Areas for microanalysis of the coating after the second electrolysis (1, 2). Melt: (NaCl-KCl) - 10 wt.% NaF - 5 wt.% NdF₃. Temperature: 1023 K. Electrodeposition time: 8 hours. The cathodic current density: 5 mA cm⁻².
Probably, the presence of carbon on the substrate prevents the formation of a continuous layer of Nd-Co intermetallic compounds, and intermetallic compounds are formed only on substrate islands not occupied by carbon. Thus, to obtain continuous deposits of neodymium with cobalt, it is necessary to use the purification electrolysis.

Indeed, after the second electrolysis from the same electrolyte, the formation of a carbon film is not observed on the substrate, but crystals with a size of 2-5 microns are formed. The morphology of the coating is shown in figure 4.

Microanalysis of individual crystals on the surface of the cobalt substrate (figure 4) indicates on the formation of intermetallic compounds Co$_{17}$Nd$_2$ and Co$_5$Nd. For example, the crystal 1 is an intermetallic compound Co$_{17}$Nd$_2$ (neodymium content 21.38 wt.%), and crystal 2 is an intermetallic compound Co$_5$Nd (neodymium content 32.65 wt.%). The same results were obtained after the third electrolysis in the same electrolyte.

Thus, the electrodeposition of neodymium on a cobalt substrate from the NaCl-KCl - 10 wt.% NaF - 5 wt.% NdF$_3$ melt, using a neodymium anode and a cathodic current density of 5 mA cm$^{-2}$ and an electrolysis time of 8 hours leads to the formation film made of intermetallic compounds Co$_{17}$Nd$_2$ and Co$_5$Nd.

4. Conclusion
The electrodeposition of neodymium on a cobalt substrate in a chloride-fluoride melt NaCl-KCl -10 wt.% NaF-5 wt.% NdF$_3$ was studied. Microanalysis of the coating determined the electrocrystallization of intermetallic compounds Co$_{17}$Nd$_2$ and Co$_5$Nd on a cobalt substrate.

References
[1] Kuznetsov S A and Kalinnikov V T 2008 Glass Phys. Chem. 34 5 575–81
[2] Kuznetsov S A and Gaune-Escard M 2009 J. Nucl. Mater. 389 1 108–14
[3] Bukatova G A and Kuznetsov S A 2005 Electrochemistry (Tokyo, Jpn.) 73 8 627–9