JOINT ELECTROREDUCTION OF LANTHANUM, GADOLINIUM AND BORON IN HALIDE MELTS

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Abstract

The joint electroreduction of La, Gd and B from chloride-fluoride melts has been studied by cyclic voltametry. Based on the analysis of voltamograms the possibility of electrosynthesis of lanthanum-gadolinium borides from chloride-fluoride melts has been shown.

Keywords: joint electroreduction, lanthanum and gadolinium chloride-fluoride complexes, tetrafluoroborate-ion, high-temperature electrosynthesis, lanthanum-gadolinium borides

1. Introduction

During the last years rare-earth metals and their alloys and compounds found a broad range of applications in metallurgy, semiconductor electronics and laser technique, which is due to their unique physical and chemical properties. It is well known that lanthanum and gadolinium tetraborides are good neutron absorbers. Lanthanum hexaboride is used for the production of cathodes for charged particles accelerators, which are used in refractory metals welding. That is why the development of new effective methods for rare-earth metals compounds production is a challenge. High-temperature electrosynthesis is one of the perspective solutions for that.

Analysis of available publications shows that reliable data on the deposition of
compounds during the joint reduction of lanthanum, gadolinium and boron complex ions are missing. The goal of the present work is to study the joint electroreduction of lanthanum, gadolinium and tetrafluoroborate-ions in chloride-fluoride melts with the formation of lanthanum-gadolinium borides.

2. Experimental

In the present work, the following experimental methods were used:

a) cyclic voltametry at different scan rates (i.e. under stationary and non-stationary polarization conditions);

b) potentiostatic and galvanostatic electrolysis;

c) X-ray phase analysis.

As a solvent, the equimolar mixture of NaCl and KCl with up to 10-wt. % NaF was used. The rare-earth elements were added into the melt in the form of their dehydrated chlorides. Potassium tetrafluoroborate, before its introduction into the melt, was re-crystallized in HF-solutions, rinsed with alcohol and dried in vacuum. All operations with the salts were conducted in a dry glove box. The voltamograms were taken using a PI-50-1 potentiostat. The experiments were conducted in a high-temperature hermetically closed quartz cell in pure dry argon atmosphere. The working electrode was an indifferent silver wire. Platinum or glassy carbon served as the reference electrode. A glassy carbon crucible was used as the anode and also as container for the melt.

3. Results and discussion

3.1. Joint electroreduction of LaCl₃, GdCl₃ and KBF₄ in chloride-fluoride melts

The electroreduction mechanism of lanthanum, gadolinium and tetrafluoroborate ions in halide melts was studied by us earlier [1–3].

In Fig. 1, the voltamograms obtained in the KCl–NaCl–NaF (5 mol%)–LaCl₃–GdCl₃–KBF₄ melt at different concentrations of KBF₄ are presented. Curve 3 corresponds to the process of joint reduction of lanthanum and gadolinium ions in the chloride-fluoride melt (at potentials −(1.75-2.0)V versus the quasi-reversible platinum reference electrode). The addition of KBF₄ (∼(2.0-4.0)⋅10⁻⁴ mol/cm³) to the melt leads to the change of the character of voltamograms, both in cathodic and anodic parts (curves 4–6). The reduction wave of tetrafluoroborate ions to elemental boron appears at − (1.3-1.4)V in the cathodic part of the voltamograms. The wave of joint reduction of lanthanum and gadolinium ions is elongated along the potential axis appears at more negative potentials.

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Figure 1. Cyclic voltamograms of NaCl-KCl-NaF(5-wt. %)-LaCl₃-GdCl₃-KBF₄ melt on an Ag-electrode. 1-NaCl-KCl(1:1)-NaF; 2, 3, 4, 5, 6 - C(LaCl₃)=1.97×10⁻⁴ mol/cm³; 3, 4, 5, 6-C(GdCl₃)=2.16×10⁻⁴ mol/cm³; 4-C(KBF₄)=2.07×10⁻⁴ mol/cm³; 5-C(KBF₄)=4.13×10⁻⁴ mol/cm³; 6-C(KBF₄)=8.27×10⁻⁴ mol/cm³. Reference electrode-Pt. T=973 K.

The increase in $BF_4^-$ ions concentration (curves 5, 6) leads to a drastic change in the shape of the voltamograms, especially their anodic parts. It is very difficult to separate the individual processes of electroreduction (curve 6). When complexes of lanthanum, gadolinium and boron are present in the melt, the anodic waves shift towards more positive potentials. From the shape of the voltametric curve it can be assumed that the cathodic product is a semiconductor and the processes of lanthanum and gadolinium deposition are imposed on the boron reduction process. This character of the voltamograms can be explained by the $La-Gd-B$ alloy formation. And so, based on the analysis of the voltamograms taken in the chloride-fluoride melt it can be assumed that the electrolysis of lanthanum and gadolinium borides is possible in kinetic mode only.

Thus, the process of joint electroreduction of lanthanum, gadolinium and boron can be described by the following consecutive steps:

- electrodeposition of the more positive component (boron);
- electrodeposition of the more negative component (lanthanum and gadolinium);
- mutual diffusion of lanthanum, gadolinium and boron with the formation of different boride phases.

Hence, the results of the study in the $NaCl-KCl-LaCl_3-GdCl_3-KBF_4$ melt have shown the possibility of $La-Gd-B$ alloys electrochemical synthesis.

The electrochemical processes of lanthanum, gadolinium and tetrafluoroborate-ions reduction at a silver electrode in the chloride-fluoride melt can be presented by the following reactions:

$$BF_{x}Cl_{z}^{-} + 3e^- \rightarrow B + (4-x)F^- + xCl^-$$
$$LaCl_{6-y}F_y^{3-} + 3e^- \rightarrow La + (6-y)Cl^- + yF^-$$
$$GdCl_{6-z}F_z^{3-} + 3e^- \rightarrow Gd + (6-z)Cl^- + zF^-$$  \(1\)

$$aLa + bGd + cB \rightarrow La_aGdbB_c$$

or as gross-reaction:

$$aLaCl_{6-y}F_y^{3-} + bGdCl_{6-z}F_z^{3-} + cBF_{x}Cl_{z}^{-} + 3(a+b+c)e^- \rightarrow$$
$$La_aGdbB_c + [(c(4-x) + ay + bz)]F^-$$  \(2\)

The above results on joint electroreduction obtained by cyclic voltametry were taken as the basis for the practical realization of the high-temperature electrochemical synthesis of $La-Gd-B$ alloys.

### 3.2. Electrochemical synthesis of lanthanum-gadolinium borides

Single borides of rare-earth metals were synthesized in the works of Andrieux [4, 5] (see also review [6]). The calculation of equilibrium electrochemical synthesis diagrams has been performed by us for the $La-B$ and $Gd-B$ systems [7-9]. These calculations are performed based on the principle worked out in [10]. The experimental results presented below show a good agreement, although the influence of kinetics should be taken into account.
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The composition of lanthanum-gadolinium boride phases synthesized has been studied as a function of temperature (973-1073 K), current density (galvanostatic electrolysis: $j_{\text{cath.}}=0.05-0.3$ A/cm$^2$), potential (potentiostatic electrolysis: $E=-(1.6-1.8)$ V versus platinum reference electrode), and composition of the melt ($LaCl_3$,$GdCl_3$,$KBF_4=1:1:1$).

For the synthesis of lanthanum-gadolinium borides the molten equimolar mixture of NaCl and KCl with 5 mol. % NaF as solvent for $LaCl_3$, $GdCl_3$ and $KBF_4$, which are soluble quite well in this melt, was used.

When choosing the ratio of concentrations of $LaCl_3$, $GdCl_3$ and $KBF_4$ it should be taken into consideration that the first stage of the synthesis is the reduction of the more electropositive component – boron. The reduction of more negative components (lanthanum and gadolinium) begins after potassium tetrafluoroborate is consumed at the electrode/electrolyte interface. The optimum concentration of $KBF_4$ is $(2.0-3.0)\times10^{-4}$ mol.l$^{-1}$. Due to the instability of the cathodic product, it is not possible to obtain $La$-$Gd$ borides at higher concentrations of $KBF_4$.

We have studied the influence of potassium tetrafluoroborate concentration on the composition of cathodic deposits. Boride phases appear in the deposit at the molar ratio ($LaCl_3$,$GdCl_3$,$KBF_4=1:1:1$). Boride content in the deposit increases if the concentration of potassium tetrafluoroborate in the melt is increased.

Temperature has a significant influence on the electrosynthesis of boride phases. If the temperature is kept below 973 K, the components ($La$, $Gd$ and $B$) do not interact completely. However, $BF_4$-ion is unstable above 1073 K. The electrosynthesis of lanthanum and gadolinium borides has been performed in potentio- and galvanostatic modes. It has been found that these two modes lead not to the same results. In galvanostatic mode, the actual value of cathodic current density is known only in the beginning of the process, because the cathode surface area changes significantly during the electrolysis. In most cases, potentiostatic mode was used because voltage (potential) determines the character of deposition.

Generally, the electrosynthesis of lanthanum/gadolinium borides is determined by the following interrelated parameters: composition of electrolyte, voltage on bath, duration of electrolysis, temperature. The optimum values of these parameters are as follows:

- a) composition of electrolyte (wt. %): NaCl–40.0, KCl–51.0, NaF–3.0, $LaCl_3$–3.0, $GdCl_3$–3.0, $KBF_4$–3.0;
- b) voltage on bath 2.5-3.0 V;
- c) duration of electrolysis 45-50 min.;
- d) temperature 973-1073 K.
References