

## Joint electroreduction of lanthanum, gadolinium and boron in chloride melts

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The increasing consumption of rare-earth metals in different fields of science and technics is due to unique physical and chemical properties of these metals, alloys and compounds. It is well known that lanthanum and gadolinium tetraborides are good neutron absorbers. Lanthanum hexaboride is used for the fabrication 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 obtaining is very actual.

The high-temperature electrosynthesis is one of the perspective methods 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 absent.

In the present work the following experimental methods were used:

- i. cyclic voltammetry at different scan rates (i.e. at stationary and non-stationary polarization conditions),
- ii. potentiostatic and galvanostatic electrolysis,
- iii. X-ray analysis.

As a solvent, the equimolar mixture of NaCl and KCl with up to 10 wt. % of NaF was used. The rare-earth elements were added into the melt in the form of their dehydrated chlorides, potassium tetrafluoroborate was recrystallized before its addition. All operations with the salts were performed in a dry box. The voltammograms were registered using a potentiostat of the type PI-50-1. The investigations were conducted in a high-temperature hermetically closed quartz cell in pure dry argon atmosphere. A silver wire was used as the working electrode, while platinum or glassy carbon served as the reference electrode. A glassy carbon crucible was used as the anode and also as the container for the melt.

In the presence of lanthanum halide complexes in the melt, a one-stage reduction to metallic lanthanum is observed. The addition of gadolinium halide complexes to the melt causes the appearing of two waves in the voltammogram - the first wave corresponds to the joint electroreduction of lanthanum and gadolinium with alloy formation. In this case the increase of reduction current and shift of the wave to the area of more positive potentials is observed.

The second wave is the gadolinium reduction on the surface of the La-Gd alloy. The anodic part of the voltammogram confirms this conclusion too. So we can expect a thermodynamic mode of the La-Gd alloy electrosynthesis.

As it is known, the electroreduction of boron takes place at potentials more positive (0.4÷0.5V) than the potential of lanthanum reduction. That is why the electroreduction of La-Gd borides proceeds in a kinetic mode. The addition of  $\text{KBF}_4$  to the melt leads to the appearing of boron reduction wave at more positive potentials and to increase of the wave of joint La-Gd reduction. The latter fact can be explained by the reduction of rare-earth metals on previously deposited boron, which leads to the borides formation. At higher tetrafluoroborate concentrations the formation of boride phases only is observed. Such a conclusion is confirmed by anodic dissolution of the cathodic product. Only one anodic wave corresponding to the dissolution process of the La-Gd borides appears in the voltammogram.

The composition of the  $\text{La}_x\text{Gd}_y\text{B}_z$  phases has been studied as a function of the temperature, current density (at galvanostatic electrolysis), potential (at potentiostatic electrolysis), and composition of the melt.

Therefore, based on the cyclic voltammetry of joint deposition of La, Gd and B the possibility to synthesize of La-Gd borides has been shown. The existence of boride phases has been approved by electrolysis in the La-Gd-B system and by X-ray analysis of the cathodic product.