

## **THE ELECTROCHEMICAL SYNTHESIS OF EUROPIUM BORIDE**

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### **Abstract**

*The electroreduction of boron, europium and the electrochemical synthesis of europium boride have been investigated in NaCl-KCl-NaF(10 wt. %) melt on silver and molybdenum electrodes. The parameters of boron reduction in the chloride-fluoride melt have been obtained and the character of its joint deposition with europium has been studied.*

*Keywords:* molten salts, electrochemical synthesis, boron, europium

### **1. Introduction**

The intensive production of titanium, niobium, tantalum, thorium arouses the necessity of utilization of rare earth metals, accompanying them in mineral raw materials. Modern techniques has high claims to new materials – they should satisfy the set of physical, technological, exploitation characteristics. Europium boride is recognized in metallurgy, electronics, nuclear techniques, etc., due to its advanced electrophysical properties combined with a high melting point, excellent corrosion resistance.

Electrochemical synthesis in molten salts is a promising method for the rare earth (RE) compounds production [1]. Besides comparative simplicity and relatively low costs, this method allows obtaining of products of high purity and desirable morphology (porousless thin layers or powders with controlled grain size) out of contaminated initial

substances. Electrochemical synthesis is very rational in single crystal growing and protective film plating with characteristics controlled by the process parameters. It is invincible when plating massive samples of complex shape [2, 3].

A few attempts were made to produce RE hexaborides ( $LaB_6$ ,  $GdB_6$ ,  $CeB_6$ ) by electrodeposition in molten salts [4-8] and little efforts were taken to understand the mechanism. No investigation has been reported on *Eu-B* co-deposition in halide melts. Data on the electrochemical behavior of europium and boron could provide information for the sensible choice of parameters for europium boride electrochemical synthesis. So we ran experiments in order to learn whether europium boride could be obtained electrolytically and, if so, to study the nature of *Eu-B* high-temperature electrochemical synthesis.

## 2. Experimental

High reaction ability of both boron and europium excludes the use of hygroscopic halides of alkali metals in the supporting electrolyte. Iodides and bromides are not only sensitive to moisture, but rather expensive. *LiCl* and *KF* are the most hygroscopic of chlorides and fluorides, that is a reason why they are not advisable. The bath used for the experiments consists of equimolar sodium chloride – potassium chloride mixture with 10 weight percent of sodium fluoride and additions of sodium fluoroboride and europium dichloride.

*KCl* (99.95 %, Ultrapure Alfa) and *NaCl* (99.99 %, Suprapur Merck) were dehydrated by continuous progressive heating above the melting point under *HCl* atmosphere in a quartz ampoule. The excess of *HCl* was removed by argon.

*NaF* (chemically pure) was purified by double melt re-crystallization. First, it was placed in a glassy carbon crucible (SU-2000) and dried at 400-500 °C under vacuum, then heated up to 50 °C above the melting point under argon atmosphere and cooled down slowly (3-4 degrees/hour) to 50 °C below the melting point. The solidified salt was transferred at 120 °C to a dry glove box and the impurities were removed mechanically.

$KBF_4$  was re-crystallized from commercial product in hydrofluoric acid, washed in ethyl alcohol and dried in a vacuum box.

$EuCl_2$  was synthesized from  $Eu_2O_3$  (Johnson Matthey, 99.9 %) with thionyl chloride as chlorinating agent;  $SOCl_2$  was carried by argon through solid europium oxide at a temperature of 823 K for 6 hours. The  $EuCl_3$  obtained was then reduced to  $EuCl_2$  with twofold excess of *Zn* in a quartz ampoule put in a silica reactor, which was evacuated to a pressure of about 1 Pa. The temperature was gradually increased up to 773 K and kept for 3 hours under static vacuum. Then the temperature was increased up to 1093 K and kept for 5 hours under static vacuum.  $EuCl_2$  was separated from zinc by distillation at 1193 K. All operations with  $EuCl_2$  were performed in a glove box.

The constituents of the base melt (*KCl*, *NaCl*, *NaF*) were mixed in pre-determined ratio, then put into a glassy carbon crucible which was placed in a vacuum tight, cylindrical retort of stainless steel with a water-cooled flange and subjected to the stepwise (473, 673, 873 K) pre-heating in an electrical resistance furnace under vacuum (to  $5 \cdot 10^{-3}$  Torr). The electrolyte was then fused under argon atmosphere. The working space was shielded from the steel walls of the retort by a glassy carbon tube. Electrodes were lowered through the fittings in the flange.

The studies were performed mainly by the method of cyclic voltammetry (CV interactive) on a Voltalab-40 potentiostat with a Voltmaster 4 software.

Experiments were carried out at 1023 K, at potential scan rates from  $5 \cdot 10^{-3}$  to  $2 \text{ V} \cdot \text{s}^{-1}$ . Glassy carbon (GC), silver, molybdenum rods (2, 1, 1 mm in diameter, respectively) were used as working electrodes; the potentials were measured versus quasi-reference GC electrode and silver (*Ag/NaCl-KCl-2 wt. % AgCl*) reference electrode. GC crucible served as the counter electrode.

### 3. Results and discussion

#### 3.1. Boron in chloride-fluoride melts

There are numerous works on the mechanism of boron electroreduction in halide melts. Available literature data on chloride-fluoride melts with the excess of  $F^-$  ions indicates the process to be one-step reversible (up to  $1.0 \text{ V} \cdot \text{s}^{-1}$  polarization rate) [9-11] or irreversible [12-14], while with the lack of  $F^-$  ions the process is accompanied by preceding complex dissociation [15-17], and reaction is irreversible. It is noteworthy that boron concentration decreases with time in chloride electrolytes due to the volatility of  $BF_3$  – the product of  $KBF_4$  thermal dissociation. Sodium fluoride addition to the melt stabilizes boron concentration, that is why we used *NaCl-KCl-NaF (10 wt.%)* as working electrolyte. To minimize the effect of volatility, we performed experiments within a short time – to be clearly aware of boron content in the melt. The recent work [18] let us suppose that boron electroreduction in chloride-fluoride melts is controlled by charge transfer, but there are no kinetic data on boron discharge in the chloride melt with 10-wt. % of sodium fluoride.

It was reasonable to investigate *NaCl-KCl-NaF (10 wt.%)*- $KBF_4$  melt.

During the first two/three cycles on a GC working electrode only peak of boron electroreduction from  $KBF_4$  occurs; after a number of runs, the boron-carbon interaction peak appears [19] and in the stripping half-cycle there is a wave of carbide dissolution. On the contrary, the voltammograms recorded on a silver electrode (Fig.1) reveal the peaks of boron deposition/dissolution only (in the cathodic and anodic part of the voltammogram, respectively). So silver electrode is proven to be more convenient for boron electrodeposition study. The bunch of experimental data together with the analysis

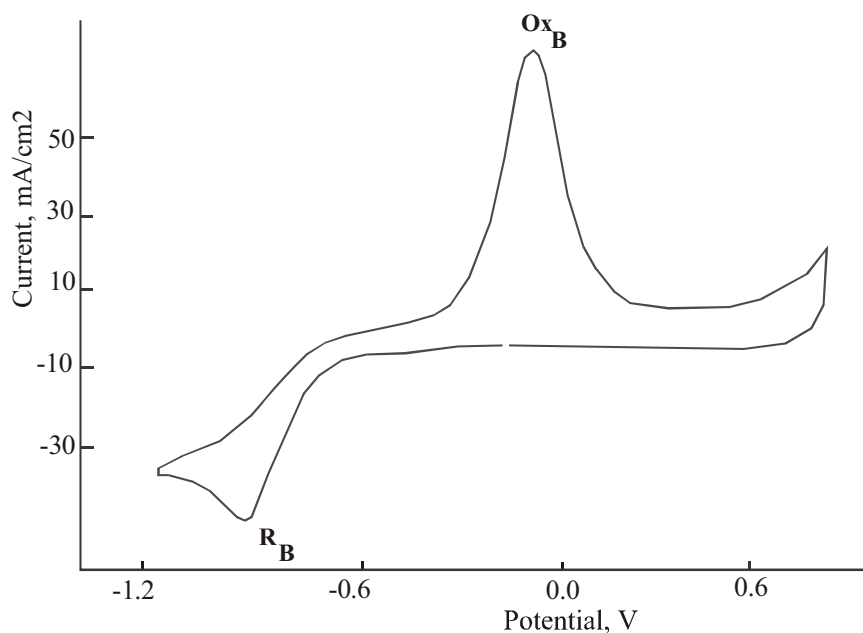


Figure 1. Cyclic voltammogram of  $\text{NaCl-KCl-NaF}(10\text{-wt. \%})\text{-KBF}_4$  melt. Working electrode - silver. Reference electrode - GC quasi-reference.  $v=0.1 \text{ V}\times\text{s}^{-1}$ ,  $T=1023 \text{ K}$ ,  $C_{\text{KBF}_4}=2.8\times 10^{-5} \text{ mol}\times\text{cm}^{-3}$ .

of diagnostic criteria of non-steady-state voltammetric measurements (rate and concentration dependencies of the peak current and potential) make it possible to conclude that boron reduction on an “inert” silver electrode occurs in a single three-electron step and it is controlled by charge transfer rate. The steady-state voltammogram recorded at the silver electrode in  $\text{NaCl-KCl-NaF-KBF}_4$  melt is characterized by a cathodic plateau. Processing the voltammogram in  $E - \log(I_r/I)$  coordinates shows that  $B(\text{III})$  reduction at low polarization rates is irreversible. In the case of irreversible electrochemical reduction, the difference between the peak and half-peak potentials is related to the parameter  $\alpha n_\alpha$  through the following dependence [20]:

$$E_{p/2} - E_p = 1.857 RT/\alpha n_\alpha F \quad (1)$$

where  $\alpha n_\alpha$  is the product of the electrokinetic transfer coefficient and the number of electrons in the stage determining the rate of the electrode process. Knowing this value, one can calculate the diffusion coefficient of boron in  $\text{NaCl-KCl-NaF}$  using the Delahay equation [21]:

$$I_p = 0.496nFCAD^{1/2}(\alpha n_\alpha Fv/RT)^{1/2} \quad (2)$$

where  $I_p$  stands for peak current density ( $\text{A}\cdot\text{cm}^{-2}$ ),  $C$  is boron concentration in the melt

( $\text{mol}\cdot\text{cm}^{-3}$ ),  $A$  is the electrode surface area ( $\text{cm}^2$ ),  $v$  is scan rate ( $\text{V}\cdot\text{s}^{-1}$ ),  $D$  is diffusion coefficient ( $\text{cm}^2\cdot\text{s}^{-1}$ ).

Being aware of the  $D$  value, one can determine the diffusion layer thickness  $\delta$  from the cathodic plateau height of the steady-state voltammogram:

$$i_d = nFCD/\delta \quad (3)$$

where  $i_d$  is diffusion limiting current density at 1023 K,  $C$  is boron concentration.

Eqs. (1-3) enable definition of the kinetic characteristics of the boron electroreduction in chloride-fluoride melt: diffusion coefficient  $D=2.4\cdot 10^{-5} \text{ cm}^2\cdot\text{s}^{-1}$ ;  $\alpha n_a=2.12$ , diffusion layer thickness  $\delta=4.9\cdot 10^{-2} \text{ cm}$ .

### 3.2. Europium(II) in chloride-fluoride melts

Europium is one of the elements whose electrochemistry is not yet clear due to a very high reduction potential. In Refs. [22-23] the electrochemical and thermodynamic properties of *Eu(III)* and *Eu(II)* in *NaCl-KCl* melt were reported. Herein we studied the electrochemical behavior of divalent europium in *NaCl-KCl-NaF(10 wt.%)*.

Since at elevated temperatures europium interacts with traditional electrode materials yielding alloys/carbides, a negative opinion about platinum, copper, silver, nickel, glassy carbon working electrodes is expressed [23]. To avoid mistakes in electrode reaction interpretation, molybdenum, which does not form intermetallic compounds and has low interdiffusion coefficient with europium, was used.

Molybdenum working electrode was used in this part of the work. There is no clear peak of europium reduction on the ascending section of the cathodic part of voltammogram (Fig.2). Europium discharges at high negative potentials together with alkali metal ions, which is in agreement with the data reported in Refs. [23,24], but a sharp anodic peak of *Eu* dissolution is observed. That peak grows up when europium concentration is higher in the electrolyte.

### 3.3. Joint electrodeposition of europium and boron

Due to considerable difference of boron and europium reduction potentials, their co-deposition is predicted to occur in "kinetic regime" [25]. The compatibility of both boron and europium with different electrode materials dictated the choice of the working electrode. Silver was tested (the most suitable material for boron) and molybdenum (the best for europium) electrodes, and *Ag* is preferred because voltammograms on a silver electrode are less "wavy" and more reproducible when both europium and boron are introduced into the melt.

We started experiments from the boron-containing melt, because boron reduction-oxidation peaks are clearly detectable on the curve, and they monitor the transformation of the voltammogram in the course of *B/Eu* molar ratio variation.

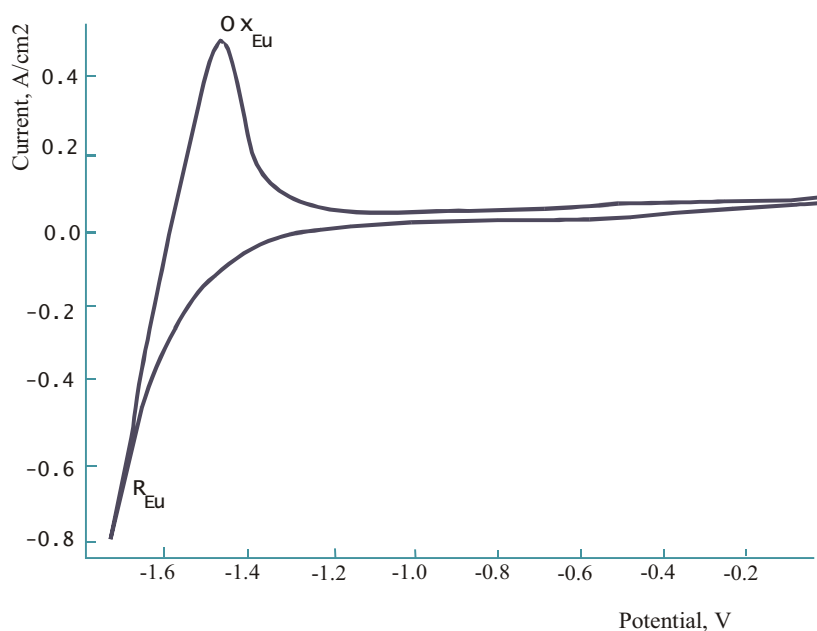


Figure 2. Cyclic voltammogram of NaCl-KCl-NaF(10-wt. %)-EuCl<sub>2</sub> melt. Working electrode - molybdenum. Reference electrode - GC quasi-reference.  $v=0.1 \text{ V}\cdot\text{s}^{-1}$ ,  $T=1023 \text{ K}$ ,  $C_{\text{EuCl}_2}=8\times 10^{-4} \text{ mol}\times\text{cm}^{-3}$ .

Even the first addition of europium dichloride to KCl-NaCl-NaF-KBF<sub>4</sub> melt causes the noticeable diminishing of both boron reduction (R<sub>B</sub>) and oxidation (Ox<sub>B</sub>) peaks (Fig.3). At the same time, new waves (R<sub>Eu</sub>, Ox<sub>Eu</sub>, R<sub>B-Eu</sub>, Ox<sub>B-Eu</sub>) appear in the voltammograms recorded at 0.1 V·s<sup>-1</sup>. The tendency of boron peaks degradation and new waves growth stays when increasing Eu/B ratio (from 0.1 to 1.0) in the melt, which implies the formation of a B-Eu compound (R<sub>B-Eu</sub>) on the working electrode. At B/Eu=1 boron reduction and oxidation peaks almost disappear and only B-Eu compound dissolution peak remains. The oxygen content in the melt was controlled (the boron-europium co-deposition in oxohalide melt will be reported later), so the new peak could not be the contribution of oxide-ion.

Thus, the results discussed above suggest the formation (at certain Eu/B ratios) of Eu-B hetero-nuclear complexes; their discharge leads to EuB<sub>6</sub> deposition onto the electrode surface.

Europium reduction itself, as it has already been mentioned, is hardly visible in the

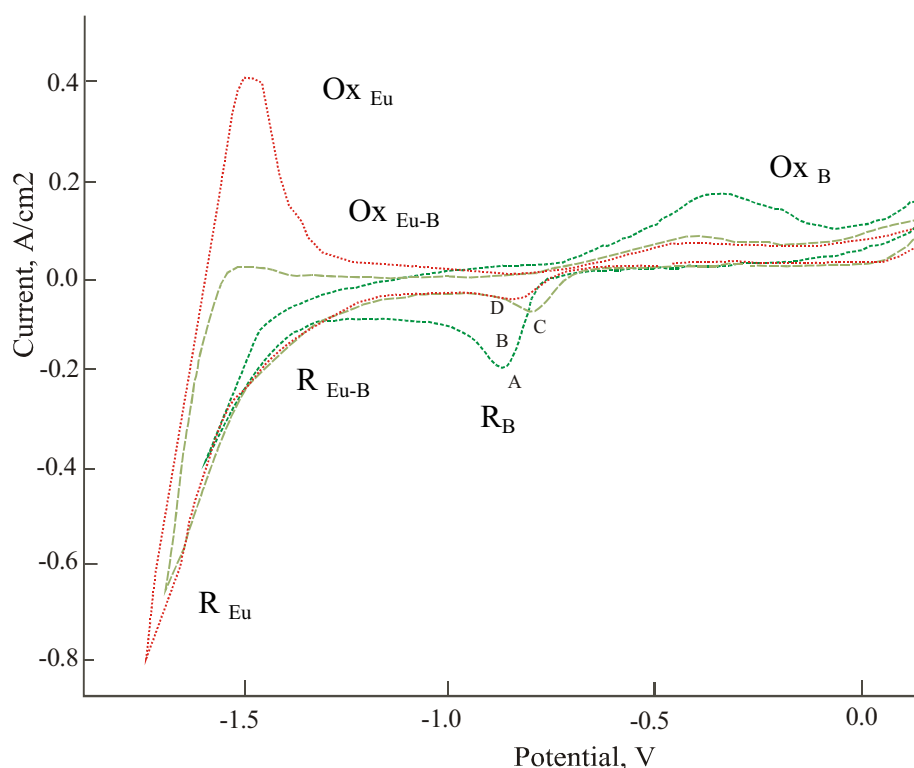


Figure 3. Cyclic voltammograms of  $\text{NaCl-KCl-NaF}(10\text{-wt. \%})\text{-KBF}_4\text{-EuCl}_2$  melt. Working electrode - silver. Reference electrode - GC quasi-reference.  $v=0.1 \text{ V}\times\text{s}^{-1}$ ,  $T=1023 \text{ K}$ , B/Eu: A-10; B-6; C-3; D-1.5,  $C_{\text{KBF}_4}=1.9\times 10^{-5} \text{ mol}\times\text{cm}^{-3}$ .

voltammogram due to its very negative potential. On the contrary, when europium is electrodeposited together with boron, the wave of the new substance deposition ( $R_{\text{B-Eu}}$ , Fig. 4) and the corresponding dissolution peak in the reverse run  $\text{Ox}_{\text{B-Eu}}$  are very distinct at low polarization rates (0.05, 0.02 V/s). The lower is the scan rate, the better the reproducibility of the voltammograms of  $\text{NaCl-KCl-NaF}(10\text{-wt. \%})\text{-KBF}_4\text{-EuCl}_2$  melt is, which is probably due to more complete dissolution of the phase formed on the electrode during the cathodic half-cycle.

A silver electrode is declared in the previous chapter to be unsuitable for europium electroreduction studies, but in the case of its joint electrodeposition with boron this restriction is cancelled. The large depolarization value of europium hexa-boride formation eliminates the *Eu-Ag* interaction, because europium electroreduction occurs on the  $\text{EuB}_6$  surface.

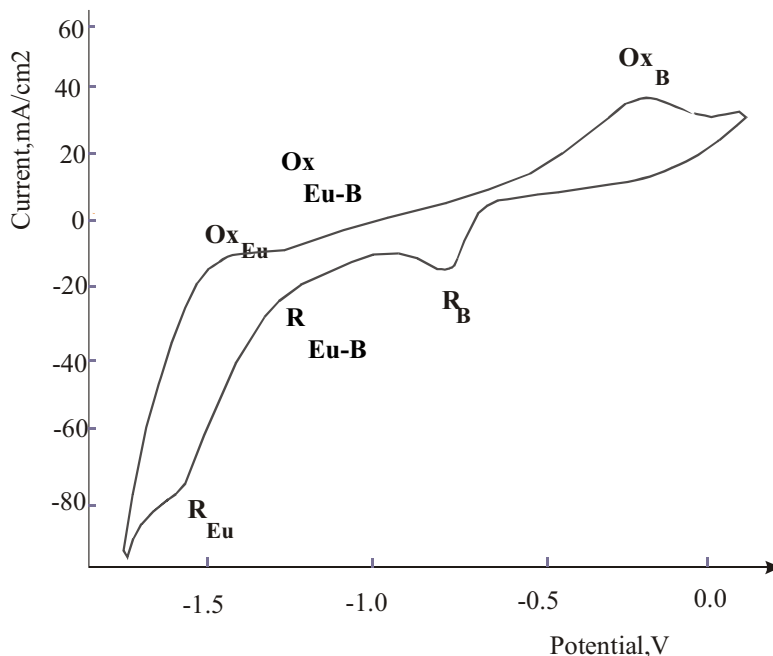


Figure 4. Cyclic voltammogram of  $\text{NaCl-KCl-NaF}(10\text{-wt. \%})\text{-KBF}_4\text{-EuCl}_2$  melt. Working electrode - silver. Reference electrode - GC quasi-reference.  $v=0.05 \text{ V}\times\text{s}^{-1}$ ,  $T=1023 \text{ K}$ ,  $C_{\text{KBF}_4}=2.8\times 10^{-5} \text{ mol}\times\text{cm}^{-3}$ ,  $B/\text{Eu}=3$ .

#### 4. Conclusions

The deposition of boron and europium (both individually and jointly) in equimolar  $\text{NaCl-KCl}$  melt with 10 wt. % of  $\text{NaF}$  has been studied by cyclic voltammetry. The diffusion coefficient of  $B(\text{III})$ , electrokinetic transfer coefficient and diffusion layer thickness were obtained for the process of boron electrodeposition. The conditions for joint boron and europium electroreduction with the formation of  $\text{EuB}_6$  have been found.

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