



Investigation of The Electrodeposit Ion Of Dysprosium Ions In Molten Halogenous Medium

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Abstract:

The electrochemical synthesis of rare earth compounds, particularly those based on dysprosium, in eutectic melts is a fascinating and highly specialized area of research. The study investigated the electrochemical co-reduction of dysprosium, boron ions in KCl-NaCl-CsCl molten salts at 823 K to synthesis dysprosium borides. Cyclic voltammetry was used to determine the optimal concentration ratio of dysprosium, boron ions for their joint electroreduction. Potentiostatic electrolysis was then used to synthesis ultra-fine powders of dysprosium borides Dy-B on tungsten electrode. The influence of electrolyte composition, temperature, current density, voltage, and electrolysis duration on the synthesis products was studied. Optimal parameters for producing high-purity Dy-B were determined

Keywords: molten salts, dysprosium, boron, tetra fluoroborate-ions, joint electroreduction, cyclic voltammetry, electrochemical synthesis, potential and galvanostatic electrolysis.

1. Introduction

The electroreduction of rare earth (RE) metals, specifically dysprosium has been explored, in molten salts. [1] Found that the tungsten electrode was indifferent to these metals, which were reduced on its surface. The synthesis of rare earth compounds in molten salts has been explored through various methods.[2] Demonstrated the precipitation of KCl and RECl₃ compounds in a LiCl-KCl eutectic, with the formation of RE₂O₃ and/or REOCl in the presence of O²⁻. [3] Reviewed the preparation of rare earth alloys, highlighting the advantages of the molten salt electrolysis method. [4-5] investigated the high – temperature electrosynthesis of dysprosium borides and silicides in chloride melts, determining optimal conditions for this synthesis. [6] Investigated the electrochemical behavior of Dy (III) and the selective formation of Dy-Ni intermetallic compounds in the same LiCl-KCl eutectic melts. [7] Furthered this work by studying the electrolytic extraction of dysprosium and the formation of various Cu-Dy intermetallic compounds in a eutectic LiCl-KCl melt. [8] Focused on the electrochemical recovery of dysprosium from a LiCl-KCl melt, with a particular emphasis on the formation of Pb-Dy intermetallic compounds. [9] Introduced an electrochemical alloying approach for the synthesis of alkaline- and rare-earth borides in molten salt, with the potential for materials purification. [10] Discussed the electrochemical synthesis of magnetic materials based on rare-earth metals in ionic melts, emphasizing the need for further research in this area.

These studies collectively contribute to our understanding of the electrochemical synthesis of dysprosium compounds and intermetallic compounds.

2. Experimental

Dysprosium chloride synthesis starts with dysprosium oxide. Dysprosium oxide reacts with hydrochloric acid to form dysprosium chloride hexa hydrate, which is then distilled by decantation. The water is

separated and dried. Anhydrous dysprosium chloride is a very hygroscopic substance. It is prepared from the hex hydrate $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ by a known method [11], where the dehydrating agent is ammonium chloride. Potassium tetra fluoroborate KBF_4 are rinsed in HF and then in ethanol and then dried. All procedures using anhydrous chlorides were carried out in an mBraun Lab star 50 glove box under argon atmosphere. The experiments were carried out in a sealed quartz cell (Figure 1) under argon atmosphere, which was purified of traces of water and oxygen, which is a necessary condition for reliability.

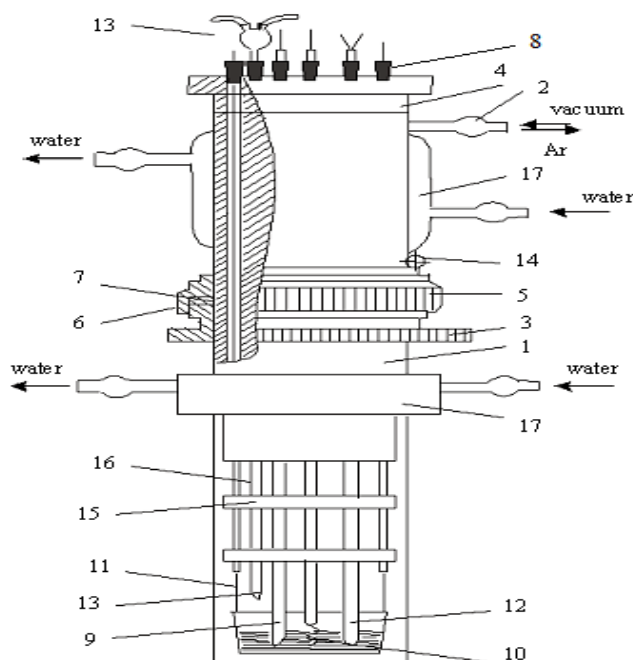


Figure. 1. Scheme of high temperature electrochemical quartz cell. 1– quartz body, 2 – union for degassing of the cell, 3 – ring threaded, 4 – PTFE bushing, 5 – steel clamping nut, 6 – vacuum rubber ring, 7 – ring PTFE, 8 – tube from the vacuum rubber, 9 – indicate electrode, 10 – reference electrode, 11 – current leads wire to the anode, 12 – thermocouple, 13 – boot device, 14 – circlip, 15 – serpentine washers, 16 – porcelain tube, 17 – cooling casing

A tungsten needle electrode ($d = 1.0 \text{ mm}$) was used as the working electrode in the three-electrode cell. A quasi-reversible rod electrode made of glassy carbon was used as the reference electrode. The use of a glassy

carbon quasi-electrode helps to avoid the use of oxygen junctions. Oxide ceramics are incompatible with halide melts containing rare earth ions. Quasi-stationary glassy carbon reference electrodes are obviously a compromise electrode, determined by the redox potentials involving the various components of the molten salt. Therefore, their parameters depend on the composition and temperature of the melt. Quasi-stationary glassy carbon reference electrodes were used in our study [12] and in the previous study of the authors [13] for chloride and chloride-fluoride melts. A glassy carbon crucible was used as anode and container for the melt. Electroreduction of dysprosium and tetra fluoroborate ions, the results were examined using cyclic voltammetry. The current-voltage dependence was determined by the following equation the electrochemical complex Autolab PGSTAT 30 (Ecochemie, Holland), coupled to a computer.

Eutectic mixture of NaCl – KCl – CsCl was used as solvent. It was dating the chloride was previously recrystallized and dried in vacuum at 423-472 K and subsequently melted in an argon atmosphere. The electrodes used for the experiments were mechanically cleaned with fine sandpaper and then polished [14]. The phase composition was determined by X-ray analysis using DRON-6 and laser device for analyzing the sizes of ultra-small particles (Analysette 22 Nanotech Plus).

3. Results and Discussion

3.1. Study of the common electrolytic reduction process of boron and dysprosium

In order to investigate the possibility of electro synthesis pure dysprosium borides we studied the co-electrolytic reduction process of boron and dysprosium in halide melts.

In our previous study [15], it was shown that tungsten is the most insignificant matrix for electrodepositing dysprosium. Therefore, we led study of the combined electroreduction of dysprosium chloride ion complexes and tetra fluoroborate ions at a tungsten electrode. The combined electroreduction of dysprosium chloride ion complexes and tetra

fluoroborate ions was carried out in a sealed quartz cell (Figure 1) in a pure argon atmosphere in a NaCl-KCl-CsCl melt at 823 K. The cyclic voltammogram corresponding to the combined electroreduction process of boron and dysprosium complexes is shown in Figure2.

Curve two (Fig 2) corresponds to the reduction potential of the dysprosium halide ion complex at a potential of - (2.80 –2.95) V relative to a quasi-reversible glassy carbon electrode. The addition of tetra fluoroborate ions to the melt changes the cathodic and anodic parts of the voltammogram (curves 3-5). The cathodic wave extends along the potential axis. The anodic dissolution of the cathodic product corresponds to several waves, depending on the concentration of tetra fluoroborate ions at a constant DyCl_3 concentration.

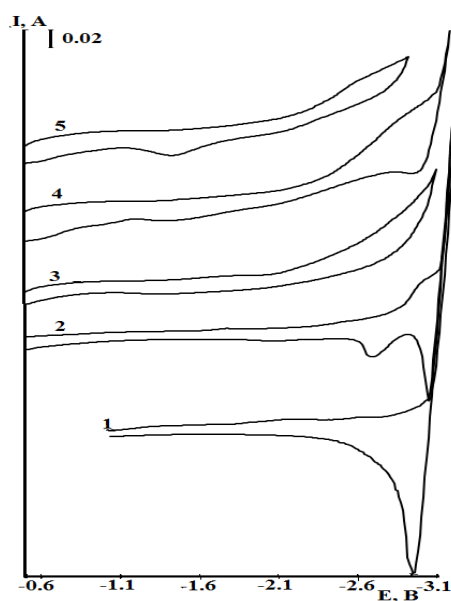


Figure 2. Cyclic Voltammograms of NaCl - KCl - CsCl - KBF_4 - DyCl_3 melt at 823K on tungsten electrode. 1: $\text{C}(\text{DyCl}_3) = 2.4 \times 10^{-4} \text{ mol/cm}^3$, 2: $\text{C}(\text{KBF}_4) \times 10^{-4} \text{ mol/cm}^3$: 1, 2 – 0; 3 – 2.4; 4, 5 – 7.2, scan rate = 0.07 V/s.

The Current – voltage curves of the KCl-NaCl-CsCl-DyCl₃-KBF₄ melt (Fig.3) at various return potentials allow us to trace the correspondence between the cathodic and anodic branches of the voltammograms.

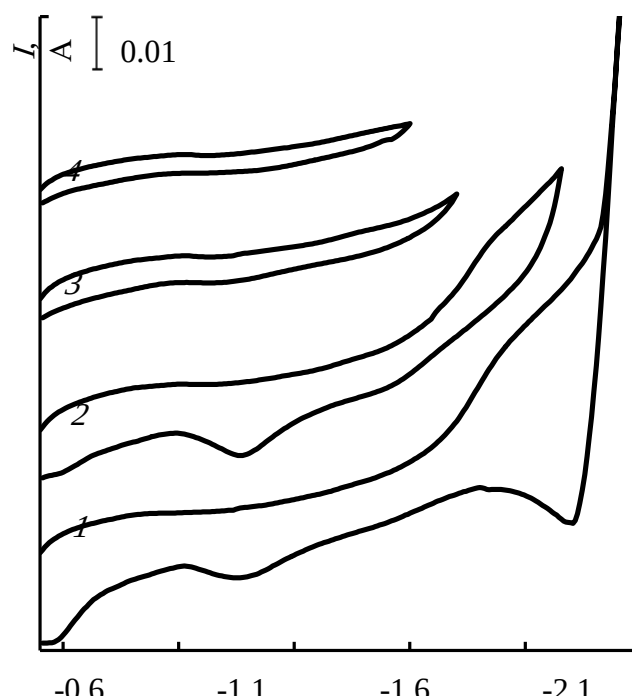


Figure 3. Cyclic Voltammograms of NaCl–KCl–CsCl–DyCl₃–KBF₄ melt at 823K on tungsten electrode, $S_w = 0.34 \text{ cm}^2$. 1 – $C(\text{DyCl}_3) = 2.4 \cdot 10^{-4} \text{ mol/cm}^3$, 2 – $C(\text{KBF}_4) = 7.2 \cdot 10^{-4} \text{ mol/cm}^3$, scan rate = 0.07 V/s. Different reverse potentials, E, V: 1 – 3.1; 2 – 2.75; 3 – 2.3; 4 – 2.1

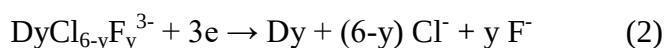
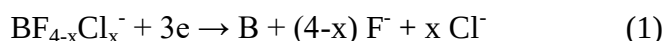
The pre-wave observed on the voltammograms before the wave for pure dysprosium recovery corresponds to the deposition of dysprosium on the boron surfaces. The observed depolarization in the deposition of dysprosium is associated with the interaction between dysprosium and boron.

Based on our investigations, it can be concluded that the electrochemical synthesis of dysprosium borides occurs only in the kinetic

regime. Consequently, the electrochemical synthesis process can be represented by the following successive stages:

1. Reduction of the more electropositive component (boron).
2. Reduction of the more electronegative component (dysprosium) on the pre-deposited boron surface.
3. Diffusion of dysprosium and boron to form the different boride phases.

The electrochemical processes occurring during the formation of dysprosium borides can be represented by the following equations:



3.2 Electrochemical Synthesis of Dysprosium Borides

We investigated the influence of temperature, potential, and the concentrations of synthesis components on the composition of the dysprosium borides phases during potentiostatic electrolysis.

The electrosynthesis of ultra-dispersive dysprosium borides was carried out in a molten mixture of NaCl – KCl – CsCl – DyCl₃ – KBF₄ at 823 K on a tungsten electrode within the potential range of -3 V to a quasi-stationary glass-carbon reference electrode.

The individual phase of boron, higher boride DyB₆ (Fig.4, 6), and the mixture of phases, including DyB₄ (Fig.5, 7), were obtained depending on the composition and synthesis parameters.

The optimum concentration of KBF₄ for the synthesis DyB₆ and DyB₄ was found to be around $(1.0 - 3.0) \times 10^{-4} \text{ mol/cm}^3$.

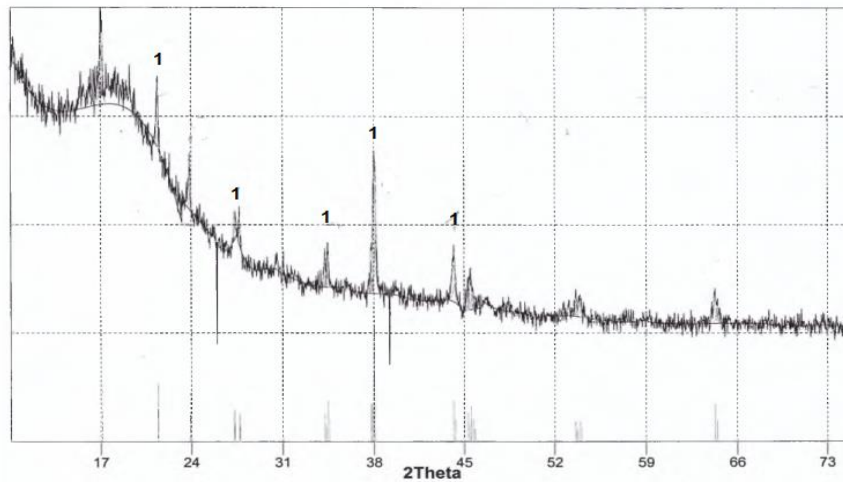


Figure 4. Radiographs of DyB_6 Powder. $E = -3$ V, Electrolysis Time 120 minutes, $T = 823K$, the substrate – Tungsten. 1 – DyB_6

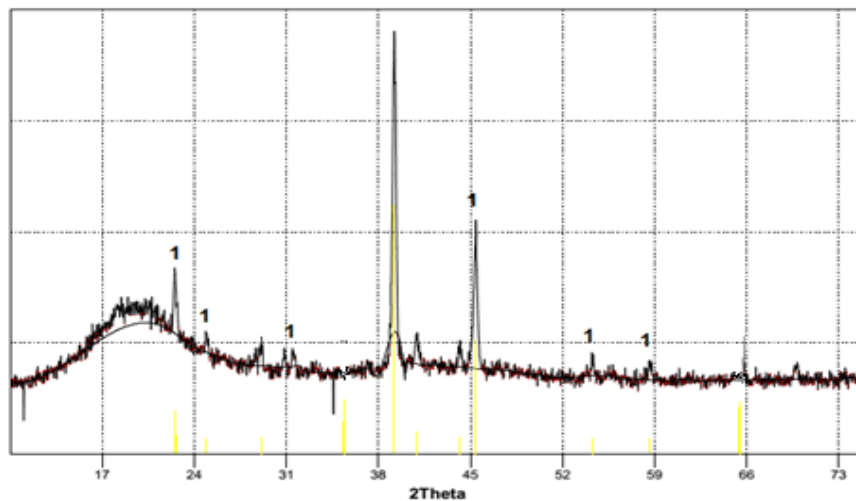


Figure 5. Radiographs of DyB_6 Powder. $E = -2.85$ V, Electrolysis Time 60 minutes, $T = 823K$, the substrate – Tungsten. 1 – DyB_4

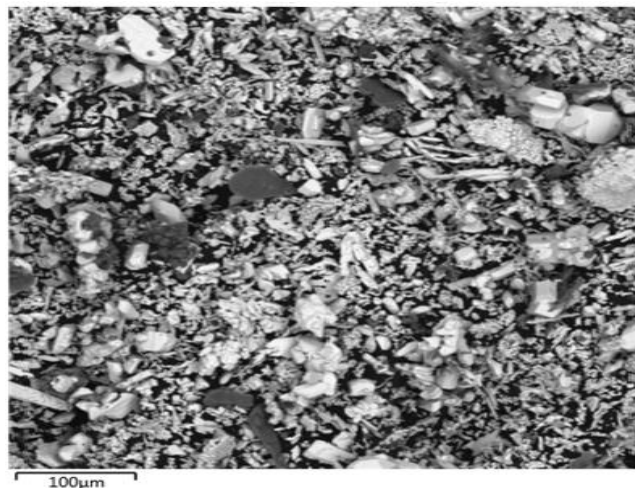


Figure. 6. SEM of DyB_6 sample obtained by potentiostatic electrolysis from the $KCl-NaCl-CsCl-DyCl_3-KBF_4$ melt. $E = -3\text{ V}$, Electrolysis Time 120 minutes, $T = 823K$, the substrate – Tungsten (W)

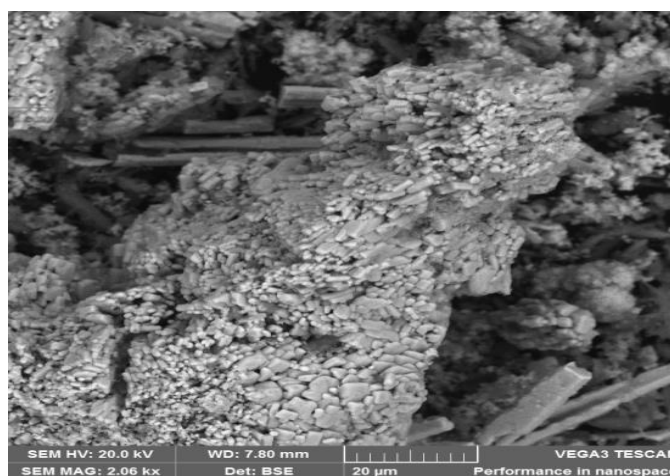


Figure. 7. SEM of DyB_4 sample obtained by potentiostatic electrolysis from the $KCl-NaCl-CsCl-DyCl_3-KBF_4$ melt. $E = -2.85\text{ V}$, Electrolysis Time 60 minutes, $T = 823K$, the substrate – Tungsten (W)

The electrochemical synthesis of dysprosium borides was investigated, with a focus on the influence of KBF_4 concentration and temperature.

At a molar ratio of $\text{DyCl}_3:\text{KBF}_4 = 1:1$, the cathode deposit started containing boride phases. Increasing the KBF_4 concentration up to a 1:3 ratio led to the formation of the higher boride DyB_6 .

The optimal temperature range for the synthesis was found to be 823-1073K. At temperatures above 1073K, BF_4^- ion becomes thermally unstable.

Both potentiostatic and galvanostatic electrolysis modes were explored. Potentiostatic mode was preferred as it better controls the deposition mechanism and reaction.

The optimal voltage range was -2.85 to -3 V, and the optimal duration of electrolysis was 60 -120 minutes at 823K.

The synthesized powders were ultra-dispersive, with the higher boride DyB_6 being the predominant phase under the optimal conditions.

The duration of the electrosynthesis also had a significant impact on the composition of the cathode deposits, as shown in the provided table 1.

Table 1. The Parameters of Electrochemical Synthesis, T= 823K

Electrolyte composition, wt. %	Voltage, E, V	Time, min	Cathode	Phase
1. Molar ratio $\text{DyCl}_3:\text{KBF}_4 = 1:3.2$				
NaCl – 18.12; KCl – 20.91; CsCl – 51.91; DyCl_3 – 3.62; KBF_4 – 5.44	- 2.70	45	W	DyB_2 , DyB_{66}
2. Molar ratio $\text{DyCl}_3:\text{KBF}_4 = 1:4$				
NaCl – 16.51; KCl – 19.05; CsCl – 47.29; DyCl_3 – 5.97; KBF_4 – 11.18	- 2.90	60	W	DyB_{66}
3. Molar ratio $\text{DyCl}_3:\text{KBF}_4 = 1:3$				
NaCl – 18.02; KCl – 20.79; CsCl – 51.62; DyCl_3 – 4.02; KBF_4 – 5.55	- 2.85	60	W	DyB_4 , DyB_{66}
4. Molar ratio $\text{DyCl}_3:\text{KBF}_4 = 1:3$				
NaCl – 16.75; KCl – 19.32; CsCl – 47.96; DyCl_3 – 6.66; KBF_4 – 9.31	- 3.00	120	W	DyB_6

After electrolysis, the boron and dysprosium were found to be extracted from the melt almost completely, requiring replenishment of the melt composition for continued operation.

The phase composition of the "cathode-salt pears" (Fig. 8) was identified by X-ray analysis using a DRON-6. The yield of the phase DyB_6 is 0.20–0.30 g/A.Hour, and the yield of the phase DyB_4 is 0.15 - 0.2 g/A.Hour, with a specific surface area of 5–10 m^2/g .



Figure 8. "Cathode-salt pear"

The work focused on the treatment of the cathode deposit. The best option for powder washing was found to be washing in distilled water, post-treatment with ammonium hydroxide solution and further washing with distilled water by decantation, centrifugation, and double-distilled water.

4. Conclusions

The electroreduction of dysprosium and tetrafluoroborate ions was carried out in KCl-NaCl-CsCl melts at 823K on tungsten electrode. The analysis of voltammograms showed that the electroreduction process has a kinetic mode due to the different reducing potentials of boron and dysprosium.

Synthesis of ultra-dispersive powders of dysprosium borides was carried out by potentiostatic electrolysis in molten eutectic KCl-NaCl-CsCl with DyCl_3 and KBF_4 . Optimal parameters for DyB_6 synthesis were found.

5. References

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