The High-Temperature Electrosynthesis of Dysprosium Silicides in Chloride Melts

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Abstract

Abstract: In this work results of joint fluorosilicate and dysprosium-ions electroreduction and determination of high temperature electrochemical dysprosium silicides synthesis conditions are presented. The electroreduction of dysprosium and silicon ions was carried out in KCl–NaCl melts at the 973K on tungsten electrodes by the linear and cyclic voltammetry.

As a result of these researches the optimal concentration ratio of dysprosium and silicon ions and anion composition in melts were established for the joint Dy and Si electroreduction. The analysis of voltammograms showed that the electroreduction process of investigated systems have a kinetic mode. Synthesis of ultra-disperse powders of dysprosium silicides was carried out by potentiostatic electrolysis in molten equimolar KCl–NaCl with $DyCl_3$ and K_2SiF_6. Electrolysis was carried out on tungsten electrode in the range of -2.2 to -2.4 V relatively of the quasi-stationary glass-carbon electrode. The electrosynthesis can be represented as sequence stages: an allocation of the more electropositive component (Si); an allocation of the more electronegative component (Dy) on deposited silicon surface; the diffusion of dysprosium and silicon with formation of silicide phases. The influence of the electrolyte composition, temperature, current density, voltage, electrolysis duration on synthesis products was studied. Optimal parameters for dysprosium silicide $DySi_{1.4}$ synthesis were found.

Keywords: Molten Chlorides, Dysprosium Chloride, Hexafluorosilicate-ion, Joint Electroreduction, Linear and Cyclic Voltammetry, Dysprosium Silicides, Potentio- and Galvanostatic Electrolysis, High temperature Electrosynthesis.

1. INTRODUCTION

Application area of dysprosium and dysprosium compounds application is very large. It is excellent alloying component of zinc alloys; for example, the addition of dysprosium to metallic zirconium improves the manufacturability of zirconium and increases the capture cross section for thermal neutrons. Dysprosium borides, borates, oxides and hafnates are used in the nuclear industry as an active neutron captures material (coatings, enamels, paints, control rods). The capture cross section of the natural mixture of dysprosium isotopes is about 930 barns [1–5].

Electrochemical processes for metals (electroreduction, refining, electroplating coating and electrocrystallization) in molten salts have several advantages in comparison of processes in aqueous solutions (for example, higher efficiency of electrolysis, reduced energy consumption, higher speed of electrodeposition and better deposit characteristics [6].

The electroreduction from the molten salts is a specific method for synthesis refractory metals, actinides and rare earth metals compounds [7]. The method has many ways of control of electrolysis products (great variety of background solvent, a variety of chemical and electrochemical characteristics of process and a wide temperature range).

Electrolysis from molten salt is more perspective method for dysprosium borides synthesis [8]. Electrolysis was carried out in graphite crucibles, serving both the anode and cathodes were made from graphite or molybdenum. The electrolysis was carrying out in Dy2O3–2B2O3–MgO–MgF2 mixture at 1223K–1273K, U = 3.0–15.0 V, i = 0.3–3.0 A/sm2.

As it was noted in work [8] the obtaining of the individual boride phase is practically impossible or very difficult. The disadvantages are also high temperature of synthesis and complexity of the product separation from the molten electrolyte due to the low solubility of borates and fluoride, contamination by-products, such as borates.

The results of investigations which are presented in the work are part of research series and were devoted to the studying of dysprosium silicides electrosynthesis. The objective of our study is the obtaining of pure ultra-

dispersive DySi1.4, increasing of synthesis rate of the target product from the molten electrolyte and reduced of the energy consumption.

2. EXPERIMENTAL

The initial reagent for dysprosium chloride synthesis was dysprosium oxide Dy2O3. Dysprosium oxide was converted into dysprosium chloride hexahydrate in reaction with hydrochloric acid, than was deposited by decantation with distilled water and was dried. Anhydrous dysprosium chloride is very hygroscopic compound. It was prepared from hexahydrate DyCl3·6H2O by the known method [9], where the dehydrating agent was the ammonium chloride.

Potassium hexafluorosilicate K2SiF6 was rinsed in HF, than in ethanol, after than it was dried. All operations with anhydrous chloride were carried out in glovebox mBraun Labstar 50 under the argon atmosphere. Experiments were carried out in a hermetic quartz cell (Fig. 1) under the argon atmosphere, purified from traces of moisture and oxygen, which is necessary in order to obtain reliable results.
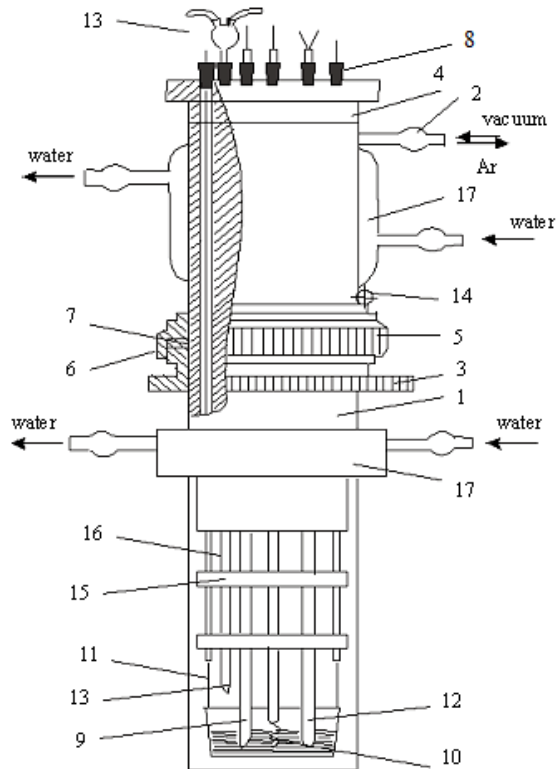
Figure. 1. Scheme of high temperature electrochemical quartz cell. 1–quartz body, 2–union for degassing of the cell, 3–ring threaded, 4–PTFE bushing, 5–steel clamping nut, 6–vacuum rubber ring, 7–ring PTFE, 8– tube from the vacuum rubber,
9–indicate electrode, 10–reference electrode,
11– current leads wire to the anode, 12–thermocouple,
13–boot device, 14–circlip, 15–serpentine washers,
16–porcelain tube, 17–cooling casing.

In three-electrode cell as a working electrode was used the tungsten ($\varnothing$ = 1.0 mm) needle electrodes. As the reference electrode was used quasireversible glassy carbon rod electrode.

The using of glass-carbon quasi-electrodes helps to avoid the using of oxygen diaphragms. Oxide ceramics are not compatible with the halide melts containing rare earth ions.

Glass-carbon quasi-stationary reference electrode, apparently, is a compromise electrode, and is determined by the redox potentials are established with the participation of the various components of the molten salts. Therefore, its parameters depend on the melt composition and temperature. Glass-carbon quasi- stationary reference electrode was used in our researches [10], and previously by the authors [11] in chloride and chloride-fluoride melts. Glass-carbon crucible was used as anode and as the container for melt.

Electroreduction of dysprosium and hexafluorosilicate ions was investigated by cyclic voltammetry. The current-voltage dependences were obtained by the electrochemical complex Autolab PGSTAT30 (Ecochemie, Holland), which was paired with computer.

Equimolar mixture of NaCl–KCl was used as a solvent. It was prepared from previously recrystallized and dried under vacuum at 423–472 K chloride with subsequent melting in the argon atmosphere. The electrodes for experiments were mechanically cleaned by the fine sandpaper, and then were polished [12].

The phase composition was identified by X-ray analysis using a DRON-6.

3. RESULTS AND DISCUSSION
3.1. Investigation of the joint silicon and dysprosium electroreduction processes

In order to explore the possibility of electrosynthesis of pure dysprosium silicides, we investigated the process of joint electroreduction of silicon and dysprosium in halide melts.

In our earlier investigations [13] it was shown that tungsten is the most indifferent substrate for dysprosium electrodeposition. Therefore we carried out

a study of joint electroreduction of dysprosium chloride ions complexes and hexafluorosilicate ions on a tungsten electrode.

Joint electroreduction of dysprosium chloride ions complexes and hexafluorosilicate ions was carried out into NaCl–KCl melt at 973K in the hermetic quartz cell (Fig. 1) under the purified argon atmosphere. In figures 2 presented cyclic voltammograms corresponding to the processes of joint electroreduction of silicon and dysprosium complexes.

Curve 2 (Fig. 2) correspond to the reduce potential of dysprosium halide ions complexes at potentials -(2.2–2.3) V relatively of quasi-reversible glass-carbon electrode. Addition of hexafluorosilicate ions into the melt changes the cathode and anode parts of voltammograms (curve 3–7), – cathode wave stretches along the potential axis. Anodic dissolution of the cathode product corresponds to several waves, which depending on the concentration of hexafluorosilicate ions at the constant concentration of DyCl3.
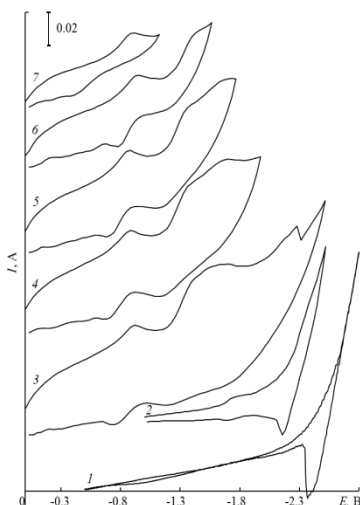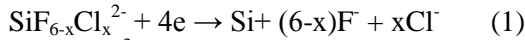
Figure 2: Cyclic Voltammograms of NaCl–KCl–DyCl$_3$–K$_2$SiF$_6$ Melt at 973K on Tungsten Electrode.1 – NaCl–KCl,
2 – C(DyCl$_3$) = 3.4·10^{-4} mol/cm^3,
3–7 – C(K$_2$SiF$_6$) = 1.7·10^{-4} mol/cm^3, scan rate = 0.07 V/s. Different reverse potentials, E, V: 3 – 2.5, 4 – 1.95, 5 – 1.75, 6 – 1.55, 7 – 1.1.

Pre-wave which observed on the voltammograms before a wave of pure dysprosium recovery corresponds to the deposited dysprosium on silicon surfaces. The depolarization, which observed in the allocation of dysprosium, we associate with interaction of dysprosium with silicon.

From our investigations it can be concluded that the electrosynthesis of dysprosium silicides is conducted only in the kinetic mode. Consequently, the electrochemical synthesis process can be represented like successive stages: reducing of the more electropositive component (silicon); reducing of the more electronegative component (dysprosium) on pre-selected silicon; diffusion of dysprosium and silicon to form the different silicide phases.

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

$$SiF_{6-x}Cl_x^{2-} + 4e \rightarrow Si + (6-x)F^- + xCl^- \qquad (1)$$
$$DyCl_{6-y}F_y^{3-} + 3e \rightarrow Dy + (6-y)Cl^- + yF^- \qquad (2)$$
$$qSi + pDy = Dy_pSi_q \qquad (3)$$

3.2. Electrochemical synthesis of dysprosium silicides

We studied the influence of temperature, potential and components concentration of synthesis on the composition of the dysprosium silicide phases at potentiostatic electrolysis.

The electrosynthesis of ultra-dispersive dysprosium silicides was carried out in a molten mixture of NaCl–KCl–DyCl3–K2SiF6 at 973K on the tungsten electrode in the range of potentials -2.8 V to relative a quasi-stationary glass-carbon electrode.

The select of electrolytic bath components was done on the basis of thermodynamic analysis and kinetic measurements of joint electrowinning dysprosium and silicon from halide melts. From the compounds of silicon and dysprosium, which do not contain oxygen, dysprosium chloride and potassium hexafluorosilicate are fairly low melting point and good solubility in equimolar KCl–NaCl melt. This supporting electrolyte was chosen because the decomposition voltage of the molten mixture KCl–NaCl more negative than the decomposition voltage of melts DyCl3 and K2SiF4 and alkali metal chlorides are highly soluble in water.

The individual phase of silicon, higher silicide DySi1.4 (Fig. 3), and the mixture of phases, including Dy5Si3 (Fig. 4) were obtained in depending on the composition and the synthesis parameters. The purpose of electrosynthesis optimization was to obtaining of higher silicide DySi1.4, with was most valuable properties. It should be noted, that electrosynthesis of Dy5Si3 and DySi1.4 phases were not described in the literature.
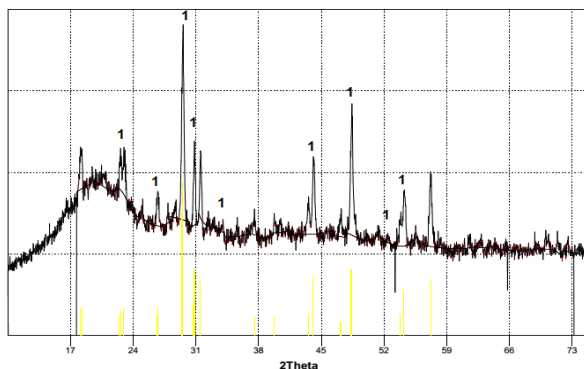
Figure. 3. Radiographs of DySi$_{1.4}$ powder. E = -2.8 V, Electrolysis Time 120 minutes, T = 973K,
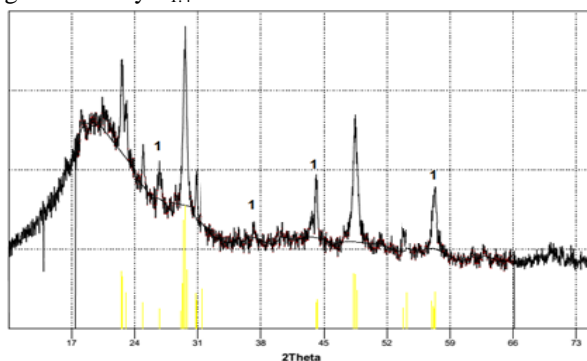the substrate – tungsten. 1 – DySi$_{1.4}$.

Figure. 4. Radiographs of Dy$_5$Si$_3$ powder. E = -2.8 V, Electrolysis time 80 minutes, T = 973K, the substrate – tungsten. 1 – Dy$_5$Si$_3$.

When we chose the concentration ratios of DyCl3 and K2SiF6, we take into account the first stage of electrosynthesis, during which the reducing of more electropositive silicon was done. Electroreduction of the dysprosium was started when K2SiF6 concentration was ended. In these temperature conditions the optimum concentration of K2SiF6 is about 8.8·10-4 mol/cm3. According to our investigations at higher concentrations of K2SiF6 the dysprosium silicides getting were complicated by instability of cathode deposit.

Temperature has the great importance at silicides electrosynthesis. We found conditions which provide completely interaction of dysprosium and silicon at

973K. It will be note that at temperature above 1073K SiF_6^{-2} ion is thermally unstable.

The dysprosium silicides electrosynthesis was carried out in potentiostatic and galvanostatic modes. It was observed that these modes are not equal. At galvanostatic electrolysis the true value of the current density is known only in the initial period of time, because during electrolysis varies significantly cathode area. In most cases we used the potentiostatic electrolysis because the voltage (potential) determines the mechanism of the reactions and control the deposition reaction. If the anode material is glass-carbon and the voltage in the bath U < -1.7 V, the cathode deposit consists mainly is silicon. Provided the voltage U = -(1.7–2.7)V the mixture of different phases (Si and Dy5Si3) was obtained. If the voltage U = -(2.8–2.9)V, the cathode deposit consists from higher silicide DySi1.4.

The duration of the electrosynthesis was affected to the composition of the cathode deposits. Data in Table show the dependence of the phase composition of the cathode deposits on parameters electrolysis.

Table

The parameters of electrochemical synthesis, E = -2.8V,   T = 973 K

Electrolyte composition, wt.%	Duration of electrolysis, min.			
	10	30-50	70	90 and more
NaCl– 37.1 KCl – 47.4 DyCl$_3$– 4.5 K$_2$SiF$_6$–11.0	Si	Si, Dy$_5$Si$_3$	Dy$_5$Si$_3$, DySi$_{1,4}$	DySi$_{1,4}$

The optimal duration of the high-temperature electrochemical synthesis for synthesis of dysprosium silicides is 90-120 minutes. Thus, the synthesis of dysprosium silicides was determined by the following interrelated parameters: the composition of the electrolytic bath, the voltage, the time electrolysis and the temperature. The optimal values of these parameters was as follows: the

composition of the melt, wt.%: $DyCl_3$ (4.0–5.0), K_2SiF_6 (10.0–11.0), the rest – equimolar mixture of NaCl–KCl; voltage -2.8 V, duration of electrolysis is 90–120 min, temperature is 973–1073K.

Thus, the essence of electrosynthesis as follows: there is a joint electroreduction of silicon and dysprosium in halide melt on the cathode and then interaction of silicon and dysprosium on the atomic level with the formation of ultra-dispersive powders of dysprosium silicide $DySi_{1.4}$.

The chemical analysis of the electrolyte after electrolysis was showed that silicon and dysprosium are extracted from the melt almost completely. For further continuing the process it is necessary correct the molten electrolytes compositions by adding salts of silicon and dysprosium.

The phase composition of the "cathode-salt pears" (Fig. 5) was identified by X-ray analysis using a DRON-6. The yield of the phase $DySi_{1.4}$ is 0.15–0.25 g/A·hour. Specific surface area of ultra-dispersive powders of $DySi_{1.4}$ is 5–10 m2/g. The yield of the phase Dy_5Si_3 is 0.10–0.15 g/A·hour. Specific surface area of ultra-dispersive powders of Dy_5Si_3 is 5–10 m2/g.

Figure. 5. "Cathode-salt pear"

Our work was focused on the cathode deposit treatment. The comparative radiographs were made before and after different options of the cathode deposit washing.

The experiments were showed that the best option of powders washing was the washing in distilled water, post-treatment with ammonium hydroxide solution

and washing with distilled water by decantation and centrifugation then by washing with double-distilled water.

CONCLUSIONS

The electroreduction of dysprosium and hexafluorosilicate ions was carried out in KCl–NaCl melts at the 973K on tungsten electrodes by cyclic voltammetry.

The analysis of voltammograms showed that the electroreduction process of investigated systems has a kinetic mode because reducing potentials of silicon and dysprosium is very different.

In results of this research were found that under certain conditions, the concentrations of dysprosium and silicon and certain anionic composition of the melt is possible of their joint electroreduction.

Synthesis of ultra-disperse powders of dysprosium silicides was carried out by potentiostatic electrolysis in molten equimolar KCl–NaCl with DyCl3 and K2SiF6.

Electrolysis was carried out on tungsten electrode in the range of -2.6 to -2.8 V relatively of the quasi-stationary glass-carbon electrode. The influence of the electrolyte composition, temperature, current density, voltage, electrolysis duration on synthesis products was studied. Optimal parameters for dysprosium silicide DySi1.4 synthesis were found.

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