UDC 541.135:620.193:669.295

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STRUCTURE AND ELECTROCHEMICAL BEHAVIUR MOLTEN HALOGENATED SYSTEMS, CONTAINING GADOLINIUM IONS

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There are considered structure and state of gadolinium ions in chloride, fluoride, chloride-fluoride, fluoride and halogenide-oxide melts were. There are analyzed the features and patterns of electrode processes of gadolinium electrodeposition from a different molten salt systems. It is shown that gadolinium ions exist in ionic melts in the form of stable halogenide complex ion. Patterns of electroreduction of complex gadolinium ions mainly are determined by the electronic structure and energy characteristics of the formative complexes.

Key words: gadolinium, melt, chlorides, fluorides, electroreduction, electrodeposition

With every year interest of researchers and demand of consumers grows to gadolinium and connections on its basis, that explained by the variety of their unique properties.

In work [1] it is reported that trichlorides rare-earth metals (REM) in the crystalline state, from a lanthanum to gadolinium inclusive, are isostructuric and have a hexagonal structure C_{6h}^{2}. Fusion of trichloride of gadolinium consists of the mutilated octahedrons $GdCl_6^{3-}$ which are incorporated by connection of bridge type through the chlorine anions.

In work [2] it is specified on existence in molten $GdCl_3$ as base units of cluster dimers and more polymerization complex anions.

By the different methods of researches it is confirmed, that in fusion of chloride of gadolinium and in the system $GdCl_3$-$MeCl$ appear durable complex groupments with the large number of ligands.

In work [3] a criterion on which it is possible to judge formations of complex connections about possibility is offered. At attitude of radius of cation of alkaline metal to the radius of lantaanide ion less than 0.7 connection does not appear, at the size of the indicated relation to 1.4 - $MLnF_4$ appears, and at its size higher than 1.4 - M_3LnF_6. Thus stability of connections of type M_3LnF_6 is high enough - they melt without decomposition.

In work [4] for the electrochemical making of rare-earth metals, in particular gadolinium, the system from fusion of salts: LnF_3-MF-LiF is offered, where M is an alkaline metal.

In work [5] results researches of electrochemical behaviour of $GdCl_3$ in the molten eutecticum of $LiCl$-KCl in the range of temperature 723-823 K are presented. It is set that the ions of Gd^{3+} are recovered on a tungsten electrode in one three-electronic stage.

Multielectronic electrode and chemical reactions during the electro-selection of gadolinium and electrochemical synthesis of alloys and connections of gadolinium from more high temperature equmolar fusion of potassium and sodium chlorides are presented in works [6]. The electroreduction of gadolinium ions was studied on silver and platinum electrodes which cooperated with the distinguished metal with formation of alloys and intermetallide. This circumstance resulted in depolarization of electrode process and complicated establishment of conformities to law of electrochemical reaction at the electroreduction of chloride complexes of gadolinium.

In work [7] there is described the electroreduction of two lanthanides (*Nd* and *Gd*) in the environment of molten $LiF\text{-}CaF_2$ at a temperature 1113 and 1193 K for a neodymium and at a temperature 1213 K for gadolinium on copper and nickel cathodes. Research showed that trifluoride gadolinium recovered to the metal in an onephasic process.

In work [8] there is studied processing of exhaust nuclear fuel ($U_{60}Pu_{20}Zr_{10}Am_2Nd_{3.5}Y_{0.5}Ce_{0.5}Gd_{0.5}$) by an electrolysis in molten chloride salt on a hard aluminium cathode. An electro-affinage was executed under a direct current at a temperature 733 K on a background the eutecticum of *LiCl-KCl*. It is marked that the division of actinoidы from lanthanides is possible even at the subzero initial relation of concentrations actinoid/REM in a salt phase.

Corrosion of gadolinium and ytterbium in molten eutecticum mixture of chlorides of lithium and potassium was studied in work [9] with the use of gravimetry and method electromotive force. It was discovered that speed of corrosion for ytterbium in 3-5 times is higher, than at gadolinium in analogical conditions. Authors are mark a satisfactory concordance between experimental and theoretical data for the process of corrosion of gadolinium.

On the liquid bismuth cathode voltage-ampermetric researches of features of electroreduction of lanthanides were executed in the eutecticum of *LiF-NaF-KF*. It is marked that metallic fallouts appear at an electrolysis.

In work [10] the coefficients of diffusion of cerium and gadolinium ions are expected. In fusion of *KCl-LiCl* in the interval of temperature 673-823 K the coefficient of diffusion of gadolinium ions is described by next equation of kind

$$\log D_{Gd} = -2,78 \ \pm 0,128 \ - \frac{1670}{T} \ . \qquad (1)$$

There are considered structure, state of ions of gadolinium, boron and silicon in chloride, chloride-fluoride, fluoride, halogenide-oxygen fusions. There are analysed features and conformities to law of electrode processes of electro-selection of gadolinium from the different molten salt systems. It is shown that the gadolinium ions exist in ionic fusions as steady difficult halogenide of complex ions. Metallic gadolinium is an active metal and at electrodeposition cooperates with many electrode materials, forming alloys and intermetallic connections.

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