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ELECTROREDUCTION OF COMPLEXES OF THE BORON IN CHLORIDE-FLUORIDE FUSIONS

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Interest to the electrochemical methods for making of the boron is conditioned by both possibility of its making in the large volumes of high degree of purity and application as a component of synthesis at the high temperature synthesis of borides [1].

There are presently realized the two varieties of electrochemical making of the boron: electrolysis of oxygen-containing connections of the boron and electrolysis of it halogenated connections.

The mechanism of electroreduction of the boron was investigated in works [6-11]. The analysis of works on the study of electrochemical conduct of the boron shows that, in spite of their far quantity, a clear picture absents both mechanism and kinetics of electroreduction of the boron from halogenated fusions.

By the basic method of researches was a linear and cyclic voltamperometry; experiments carried out at a temperature 973 ± 1 K in an inert atmosphere. There are sudied fusions $K, Na/Cl, F$, containing the boron as fluoride borate sodium.

For determination of the boron used a photometric method there is based on application of carminic acid colouring of which in presence borates passes from red in dark blue. At determination of phase composition of products of electrolysis it is used a x-ray phased analysis on the diffractometer DRON-2.0 on $Cu\text{-}K_\alpha$-radiation with the wave-length of 22.8962 nonm and vanadium filter.

On voltage-ampere dependence of electroreduction process for the boron in area of potentials from – 2.35 to – 2.7 V it is looked a wave with the clearly expressed current of spades. Further polarization is accompanied by the increase of current at potentials more than 3.0 V, by the conditioned discharge of ions of alkaline metal.

To electroreduction there are subjected particles, appearing as a result of dissociation of initial complexes, to, id est. particles BF_x^{4-x}, the concentration of which in the volume of fusion is small as compared to the general concentration of the boron ions in an electrolyte. In fusion, thus, simultaneously there are two types of particles - initial complexes $BF_{4-x}Cl_x^-$ and electrochemically active particles BF_{4-x}^{x-1}. As a result of discharge of complexes of the boron there is impoverishment of near-electrode layer that is accompanied by displacement of equilibrium of reaction for dissociation toward education electrochemically of active particles.

Thermal dissociation of fluoride-borate of alkaline metals at introduction of them to chloride fusion causes formation of volatile fluorides of the boron, which, possessing subzero solubility in fusion, pass to the gas phase. It results in the decline of concentration electrochemically of active particles and corresponding diminishing of electroreduction speed of the boron. In this connection there is a necessity for the search of method stabilizing of chloride fusion, containing fluoride-borate of alkaline metal.

The calculations of coordinating number carried out on displacement of potential of peak of wave of renewal of complexes of the boron from the concentration of free ligand in fusion on equation with using of method [8,9]:

$$\frac{dE}{d\ln C} = -\frac{N\cdot R\cdot T}{\alpha_n \cdot F} \ . \tag{1}$$

where E – potential peak of wave of renewal; C – concentration of electric active particles; N – coordination number; R – universal gas constant; T – temperature of process; α_n – coefficient of transfer, F – Faraday constant.

The coordinating number N, certain on inclination of line in the coordinates ΔE, - ln C, is equal to unity. Consequently, titration process of fusion of $KC1$-$NaCl$-$NaBF_4$ the fluorine ions is tacking to the initial particle of one fluorine ion. The mixed chloride-fluoride complex for the boron is in fusion of KCl-$NaCl$, consequently, has composition BF_3Cl^-, and particle, under in fusion at surplus of F-ion, composition BF_4^-.

Introduction to the calculations correction on the concentration of constrained ligand, determined by a molar relation [B(III)] : [F^-] =1:1 does not cause the change of their results. Consequently, charts of processes of formation of the mixed chloride-fluoride complexes of the boron and reaction of thermal dissociation in a general kind it is possible to write down as follows:

– in absence of surplus fluorine-ion:

$$BF_4^- + Cl^- \Leftrightarrow BF_3C^- + F^- \ , \tag{2}$$

$$BF_3C^- \Leftrightarrow BF_3 + Cl^- ; \tag{3}$$

– in presence surplus fluorine-ion:

$$BF_3 + F^- \Leftrightarrow BF_4^- \ . \tag{4}$$

For comparison of speeds of flowing for electrochemical reactions of components of synthesis in the case of diborides titan (zirconium) – complexes of titan (zirconium) and boron - and determination taking into account this correlation of concentrations of titan (zirconium) and boron in fusion executed the calculation of constants of speed K_s on Hochstein equation:

$$K_s = 4,35\frac{i_p}{n\cdot Fc}\cdot \exp\left(\frac{\alpha_n F}{R\cdot T}E_p\right) , \tag{5}$$

where i_p – stream of peak; n – quantity of electrons, which moved in electrode process; R – universal gas constant: E_p - potential of wave peak for corresponding process.

The results of the executed researches allowed to set that a process of electroreduction of complexes of the boron is in fusions of $KC1\text{-}NaCl\text{-}NaBF_4$ and $KC1\text{-}NaCl\text{-}NaF\text{-}NaBF_4$ flows in one stage by joining of three electrons, here the stage of transfer of charge is slow. In chloride fusion fluoride-borate-ions form the mixed chloride-fluoride complexes BF_3Cl^- which pass in BF_4 at introduction in fusion of surplus fluorine ions. Because of volatility and subzero solubility of the three fluoride boron, its concentration diminishes in fusion. Stabilizing of fusion can attain by introduction to the electrolyte of surplus amount of ions of fluorine. Necessary and sufficient is a molar relation $[B(\mathrm{III})] : [F^-] = 1 : 2$. On the basis of given data the constants of renewal speed complexes of the boron are expected at a different molar relation $[B(\mathrm{III})] : [F^-]$.

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