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On the question of using solid electrodes in the electrolysis of cryolite-alumina melts. Part 2. The mechanism of passivation and conditions of stable electrolysis

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Abstract: The aim was to investigate the mechanism of passivation of polycrystalline cathodes and to justify experimentally the possibility of stable electrolysis when using solid electrodes. Under laboratory conditions, the mechanism of electrode passivation and the conditions for stable electrolysis were experimentally studied. To this end, the methods of X-ray phase analysis and electron-microscopic examination of the spent electrodes were employed. A study of the electrolysis of cryolite-alumina melts showed that, in the presence of surface micro- and microdefects on a solid cathode, a precipitate consisting of impurities and electrolyte components was gradually formed. Under the selected experimental conditions, the surface of carbon cathodes was passivated with a dense double-layer precipitate of CaB_6 and electrolyte components. Using the example of a carbon cathode containing both metallic titanium and titanium oxides, a method for eliminating surface microdefects is presented. This method consists in electrochemical borating of a carbon-titanium cathode. The conducted spectral electron microscopic and energy-dispersive analysis found that, during a 45-hour laboratory experiment at 980 °C and under a current density of 0.7 A/cm^2, the inhomogeneous surface of the cathode was homogenized with a titanium diboride layer. At stable electrolysis parameters, an aluminum layer is electrodeposited on the cathode. A complex analysis of the electrolysis conditions, the appearance of the initial and spent carbon cathodes, and the data of analytical studies confirmed that micro- and macrodefects of the electrode cause the formation of a dense layer of deposits on the cathode. The established mechanism of passivation of a carbon cathode as a polycrystalline product can be applied to all composite electrodes, including those based on titanium diboride. A logical *condition* for the practical application of solid cathodes is the development of an electrolysis process with continuous surface reconditioning to decrease the chemical inhomogeneity and microdefects of the surface across the entire technological sequence.

Keywords: electrolysis, solid electrodes, physical microdefects, chemical inhomogeneity, cathode passivation, inert anodes, wettable cathodes

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К вопросу о применении твердых электродов для электролиза криолитоглиноземных расплавов. Часть 2. Механизм пассивации и условия стабильного электролиза

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Резюме: Цель – исследование механизма пассивации поликристаллических катодов и экспериментальное подтверждение способа стабильного электролиза с применением твердых электродов. В лабораторных условиях экспериментально исследуется механизм пассивирования катодов и условия стабильного ведения процесса электролиза с привлечением рентгенофазового анализа и электронно-микроскопических исследований использованных электродов. В процессе электролиза криолитоглиноземных расплавов установлено, что при наличии поверхностной микро- и макродефектности на твердом катоде последовательно формируется осадок из примесей и составляющих электролита. В созданных условиях эксперимента поверхность углеродного катода пассивировалась плотным двуслойным осадком из CaB_6 и составляющих электролита. На примере углеродного катода, содержащего титан в металлическом виде и в виде его оксидов, представлен способ устранения поверхностной микродефектности электродов, заключающийся в электрохимическом борировании углеродтитанового катода.

Спектральным электронно-микроскопическим и энергодисперсион ным методами анализов установлено, что в течение 45-часового лабораторного эксперимента при 980°С и плотности тока 0,7 А/см^2 неоднородная поверхность катода гомогенизирована диборид-титановым слоем. При стабильных параметрах электролиза криолитоглиноземного расплава на катоде электроосажден слой алюминия. Комплексный анализ условий электролиза, внешнего вида исходных и использованных углеродных катодов, данных аналитических исследований дают основания утверждать, что формирование на катоде плотного слоя осадков провоцирует поверхностная микро- и макродефектность электрода. Установленный механизм пассивирования углеродного катода как поликристаллического изделия распространяется на любые композитные электроды, в том числе на основе диборида титана. Логичным условием применения твердых катодов является организация процессов электролиза с непрерывным восстановлением поверхности, уменьшением ее химической неоднородности и микродефектности в течение всего технологического периода.

Ключевые слова: электролиз, твердые электроды, физическая микродефектность, химическая неоднородность, пассивация катода, инертные аноды, смачиваемые катоды

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INTRODUCTION

The first part of this paper presented an extensive review of the research and inventions related to the electrolysis of cryolite-alumina melts using solid electrolytes. Among them were Hall's and Heroult's patents (1886–1892) [1–3], which described the method of electrolytic production of aluminum. Unfortunately, this method never found practical application. In 1988, the efforts of the Pittsburgh Reduction Company to implement Hall's ideas in practice led to the construction of electrolytic cells with liquid aluminum, whose surface acted as a cathode. Along with the continuous development of this technology [4–10], there were attempts to develop a technology of electrolysis of molten salts on solid electrodes, which was expected to provide decreased energy consumption, reduced environmental burden and increased specific output. Under laboratory and semi-industrial conditions, the possibility of using various types of oxygen-evolving anodes and aluminum-wetted cathodes [11–17] was studied. Along with the confirmed possibility of their use in principle, such challenges as the increased consumption of dissolving anodes, passivation of cathodes and other electrolytic process dysfunctions were noted. The proposed recommendations to increase the working temperature and correct the compositions of the electrolyte and electrode have not so far provided conditions for implementing this technology on a commertial basis.

According to numerical studies and experimental data[1], the reason for the abovementioned problems and limitations consists in the chemical and physical inhomogeneity of the surface structure of electrodes. The concentration of current on the micro-areas of surface defects causes an increase in the rate of electrode processes with the development of concentration polarization and an uncontrolled increase in voltage up to the formation of critical electrode potentials for the present simple and complex ions. At the positive electrode, this will lead in varying degrees to the release of gaseous fluorocarbons at the carbon anode and fluorine at the inert anode, with corresponding adverse consequences. At the cathode, a discharge of electronegative impurities and decomposition of electrolyte components develop, followed by surface passivation and electrolysis destabilization. These undesirable processes are highly likely when using polycrystalline or cast anodes and cathodes, thus requiring theoretical study and practical research. In this part of the paper, the consequences of electrolysis of cryolite-alumina melts at a carbon cathode, in which the

[1]Gorlanov E.S. Doping of cathodes used in aluminium electrolytic cells by a low-temperature synthesis of titanium diboride: Dissertation for the Degree of Dr. Sci. in Engineering: 05.16.02. Saint Petersburg, 2020. 391 p. / Горланов Е.С. Легирование катодов алюминиевых электролизеров методом низкотемпературного синтеза диборида титана: дис. … д-ра техн. наук: 05.16.02. СПб., 2020. 391 с.

current process is complicated by the complex composition of the electrolyte, are studied by standard physicochemical methods. This exaggerated variant of cathode passivation in laboratory conditions is interesting for the following reasons: first, by modelling the electrolysis conditions of industrial electrolytes of complex composition; second, there is a possibility of instrumental analysis of the details and mechanism of cathode passivation, and third, such studies make it possible to elaborate and assay the approaches to overcome the existing limitations in using solid electrodes for electrolytic production of aluminum. In this regard, one of the possible ways of reducing the surface heterogeneity at the micro- and macrolevel is presented, i.e., the method of borating a metal-containing cathode in trace amounts.

EXPERIMENTS AND DISCUSSION

Experiments were carried out on a laboratory setup under galvanostatic conditions at a temperature of 980 °C and an interpolar distance of 30–34 mm. A cell was used, in which a graphite crucible served as an anode, and a carbon-graphite cylinder with a diameter of 30 mm and a height of 50 mm, immersed in the electrolyte, served as a cathode.

Study of the cathode passivation mechanism. In Experiment No. 1, an original composition of electrolyte based on technical cryolite was corrected to a cryolite ratio (c.r.) 2.7, saturated with alumina (8.3 wt.% Al_2O_3) and calcium fluoride (4.6 wt.% CaF_2). Moreover, borax, in the amount of 12.7 wt.% $Na_2B_4O_7 \cdot 10H_2O$, as a boron source was added to the electrolyte. During 24 h of the experiment, the current density was maintained at 0.4 A/cm^2, and the boron content was replenished every 1 h of the experiment. In the cell, the voltage, which varied during the experiment in the range of 2.450–2.510 V with a periodic short-term increase to 4–5 V, was monitored using a voltmeter.

Following the completion of Experiment No.1, a viscous dark precipitate was found at the bottom of the crucible, and a 3–5 mm thick dense layer of solidified electrolyte which could not be cleaned with a scraper (fig. 1) was found on the submerged part of the cathode. Note that a cross-section of the 5-mm thick precipitate layer differs in contrast and density. A sample of this layer for X-ray diffraction (XRD) analysis was cut with a diamond wheel. For the same purpose, a scrape-off was made from a surface layer of the carbon cathode. The analysis results indicate that a mixture of components of electrolyte and calcium hexaboride (tab. 1) is present on the cathode surface. Neither aluminum nor Al_2O_3 or B_2O_3 as independent phases were identified in the samples of the electrolyte; however, unidentified crystalline and amorphous phases were found in amounts of 10–20 wt.%.

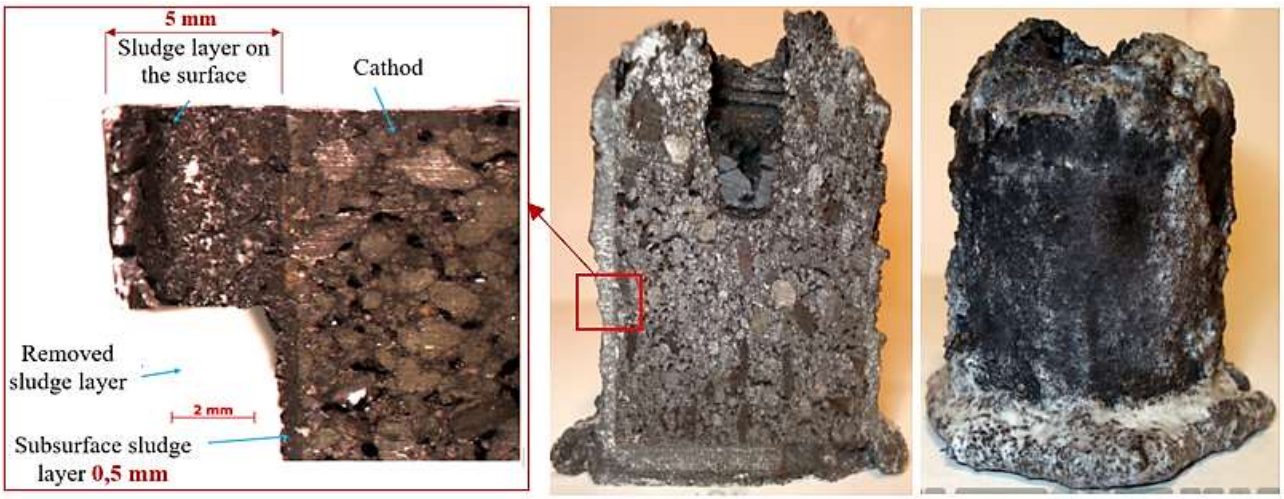

Fig. 1. The sample after removing from the cell
Рис. 1. Образец после извлечения из ячейки

Table 1. The composition of the precipitate (XRD data)
Таблица 1. Состав осадка (данные рентгенофазового анализа)

Phase	Sampling point	Content, wt.%
CaB_6	cathode surface	15.4
	precipitate	12.3
Na_3AlF_6	cathode surface	23.3
	precipitate	75.3
NaF	cathode surface	0
	precipitate	8.8
Crystalline phase	cathode surface	20–25
	precipitate	0
Amorphous phase	cathode surface	10
	precipitate	15–20

It is obvious that the compounds found, in particular, calcium hexaboride, can passivate the cathode surface and isolate access of electroactive components. In this regard, the authors undertook a study of the electrodeposition mechanism of CaB_6 which is a semiconductor having an order of magnitude higher electrical resistance (120–220 μOhm·cm) than that of titanium diboride (12–26 μOhm·cm) [18].

First, note that the decomposition of oxide and the discharge of aluminum ions on the cathode surface at 1000 °C, relative to calcium ions, has the following advantage:

$$B_2O_3 + 3/2C = 2B + 3/2CO_2, \quad E^0_{B3+/B} = -0.626 \text{ V}; \tag{1}$$

$$A1_2O_3 + 3/2C = 2A1 + 3/2CO_2, \quad E^0_{Al3+/Al} = -1.154 \text{ V}; \tag{2}$$

$$CaO + C = Ca + ½CO_2, \quad E^0_{Ca2+/Ca} = -1.607 \text{ V}. \tag{3}$$

These advantages of aluminum oxide remain before the decomposition of calcium oxide/boron oxide complexes:

$$Ca_3(BO_3)_2 + 3C = 3Ca + 2B + 3CO_2, \quad E^0_{Ca2+/Ca} = -1.297 \text{ V}; \tag{4}$$

$$Ca_3(BO_3)_2 + 3/2C = 3Ca + B_2O_3 + 3/2CO_2, \quad E^0_{Ca2+/Ca} = -1.969 \text{ V}. \tag{5}$$

Nevertheless, there is no aluminum on the cathode surface, but the CaB_6 layer is formed. The standard reason for this phenomenon may be a deficiency of aluminum ions, but the content of aluminum oxide in the electrolyte, close to saturation, remained sufficient to ensure the process. Therefore, it was assumed that the mechanism of formation of calcium hexaboride could be related to the inhomogeneous surface of the composite carbon cathode having numerous micro- and macroroughnesses, cracks, and pores. fig. 2 shows the microstructures of different portions of the carbon cathode under magnification from ×55 to ×3050.

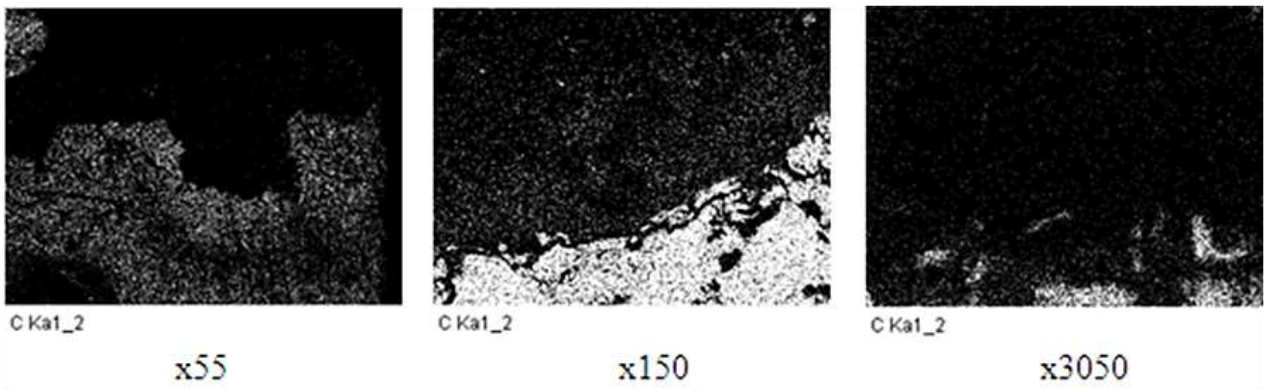

Fig. 2. Cathode surface condition
Рис. 2. Состояние поверхности катода

Given such a physical inhomogeneity, the current is concentrated on the faces and edges of the pores, point areas of microdefects. A high fluctuating current density is observed over the entire surface, approaching the limit values for boron and aluminum discharge. Accordingly, there is a high probability of the cathode potential shift to the electronegative side until the decomposition potential of calcium oxide and its complexes according to reactions (3)−(5). The effect is aggravated by an excessively high concentration of components in the electrolyte, which deteriorates the scattering properties of the melt and the microdistribution of current at microdefects [19].

Reduced adatoms of calcium and boron stabilize their state at the surface by interaction to form calcium hexaboride:

$$Ca + 6B = CaB_6. \quad (6)$$

The proposed mechanism for the formation of such precipitates was revised according to the results of scanning electron microscopy and energy-dispersive spectroscopy (SEM-EDS) on the site on the lateral surface of the cathode, undertaken to determine the location (distribution) of CaB_6 in the near-surface zone. fig. 3 below shows the macro- and microstructure of the site, including the surface crust of the electrolyte and the lateral subsurface carbon layer of the cathode. As shown in fig. 3, not the entire 5-mm layer of the precipitate was subjected to electron microscopic study, but only a thin near-cathode layer of about 0.5 mm.

As follows from the data of energy dispersive analysis (fig. 4), in the presence of calcium melt on the surface of the carbon cathode, the precipitate is formed in 2 layers. The upper layer consists almost entirely of calcium boride CaB_6. This layer extends along the scanning line up to

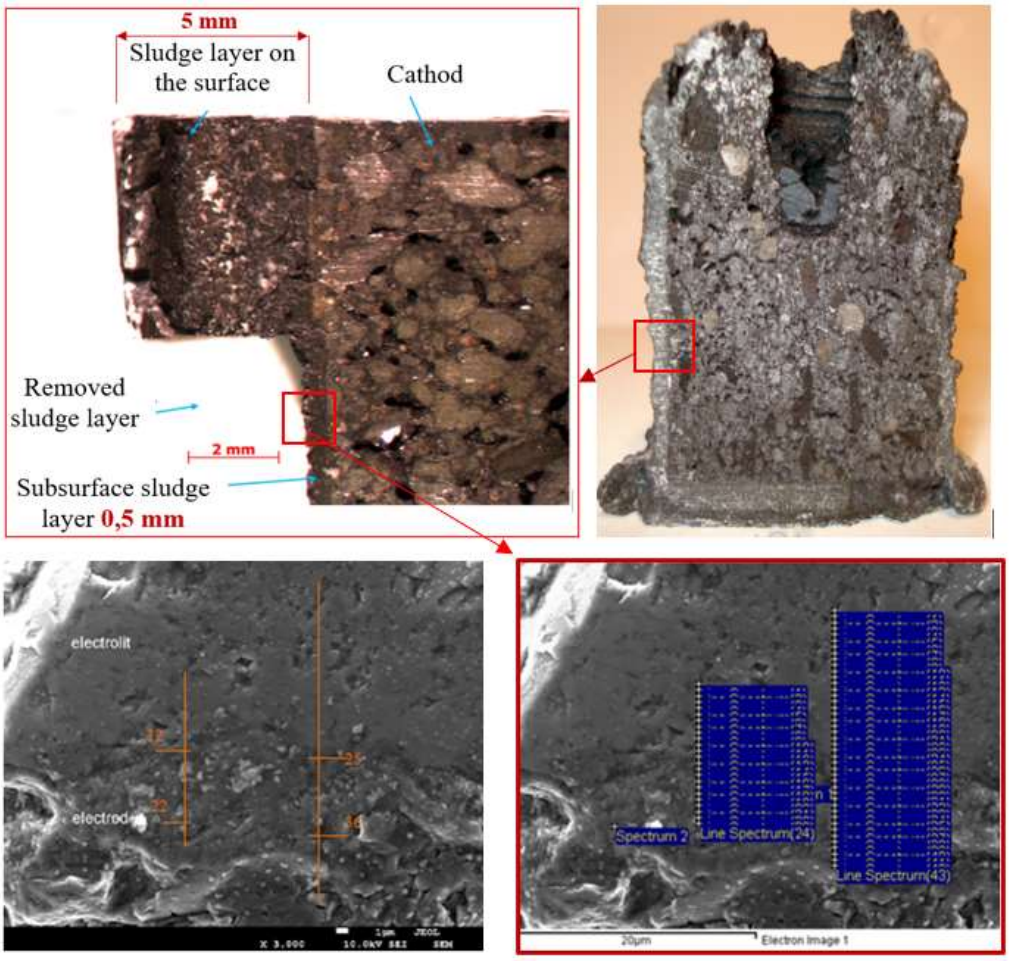

Fig. 3. Microstructure of the sample (x3000)
Рис. 3. Микроструктура образца (x3000)

point 25, after which the content of calcium (Ca) and boron (B) sharply decreases. On the contrary, the content of the electrolyte components Na, Al, F and O increases and spreads by 5–8 microns to point 36, after which the carbon content increases. In other words, a thin (about 5 μm) electrolyte layer is present between the calcium hexaboride layer and the cathode surface.

EDS mapping of the site confirms the layered structure of the melt above the cathode surface. To determine the areas of distribution of elements, the lower limit of calcium (Ca) was copied to other maps.

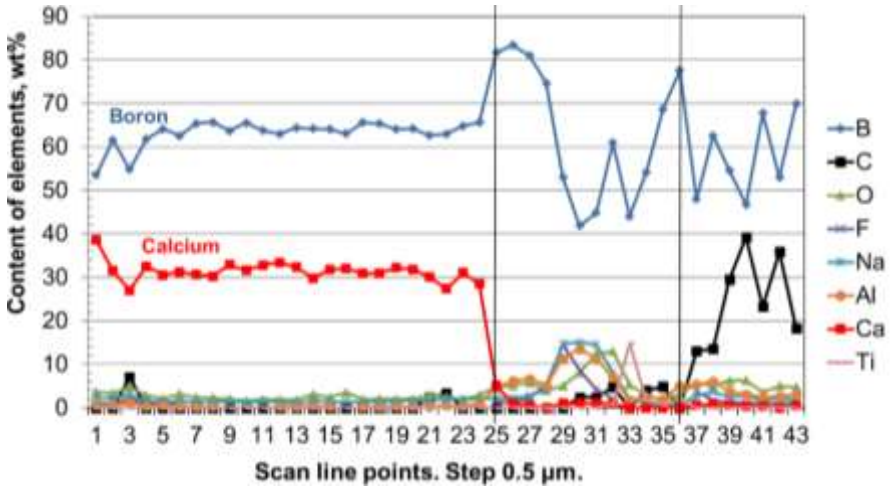

Fig. 4. EDS analysis along the line of point spectra (the first scanning line, see fig. 3)
Рис. 4. EDS-анализ по линии точечных спектров (правая линия сканирования, см. рис. 3)

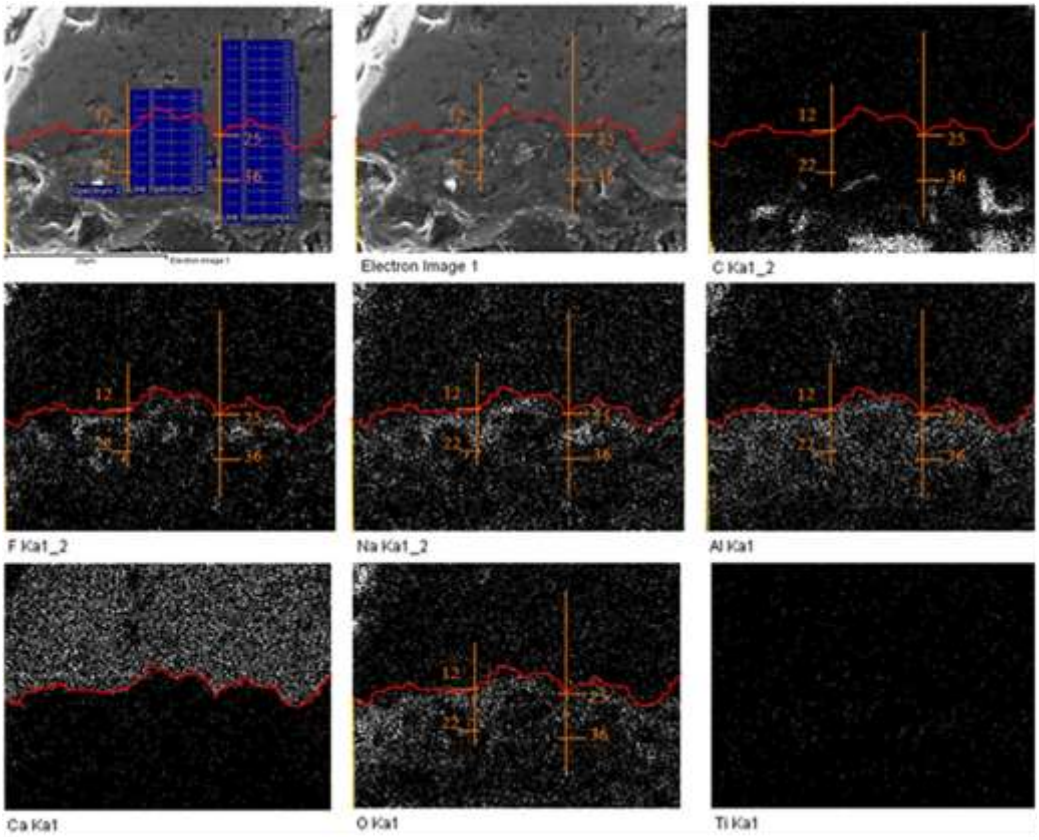

Fig. 5. EDS mapping of the site of a sample (×3000)
Рис. 5. EDS-картирование участка образца (×3000)

A sharp boundary of the calcium layer is clearly observed (there is no map for boron), adjoining the electrolyte layer, which gradually passes and is absorbed into the carbon surface. That is, there is an electrolyte interlayer between the CaB_6 layer and the carbon surface. It is obvious that this 8–10 μm layer corresponds to the diffusion layer of the cathode surface. This gives reason to believe that the discharge of boron and calcium ions from the complexes and the interaction between them occur in the thickness of the diffusion layer, i.e. in the near-cathode volume of the electrolyte, rather than on the cathode surface. It is known that bulk crystallization of compounds occurs at current densities higher than the limiting diffusion for the deposited components, or at least one of them [19]. The products of reduction and interaction are concentrated in the near-electrode electrolyte layer within the thickness of the diffusion layer from the cathode. These deposits are partially dispersed in the volume of the electrolyte and, due to the small thickness of this electrolyte layer, to the cathode surface. Thus, the electrode surface is passivated by a dense CaB_6 layer, which has more microdefects in comparison with the original carbon layer. With a deficiency or absence of electronegative impurities in the electrolyte, decomposition of the electrolyte components begins on this polarized surface of the cathode with a relatively high electrical resistance, with the formation of a layer of about 5 mm (see fig. 1). In this case, according to the XRD results (see tab. 1), crystalline and then amorphous phases are sequentially formed (probably xCaO·$y$$Al_2O_3$ and xCaO·$y$$B_2O_3$).

In the original electrolyte composition according to Experiments No. 2 and No. 3, CaF_2 additives were not used (tab. 2), which affected the composition of the passivating precipitates. Nevertheless, on the cathode surface and in the precipitates, a smaller but significant content of CaB_6 was found. This is explained by the presence of calcium in the form of its oxides or fluorides in technical cryolite with a c.r. = 1.78, which was used to prepare the original composition of the electrolyte. Thus, this effect emphasizes the significance and efficiency of physical microdefects on the cathode surface.

The given mechanism of passivation of polycrystalline cathodes is implemented to some extent when carrying out electrolysis using not only carbon electrodes but also any other polycrystalline products, including those based on titanium diboride [20]. The physical and chemical inhomogeneity of composite materials limits their use in the design of new generation electrolytic cells with drained cathodes and vertical inert electrodes. A logical way to overcome these limitations is to eliminate the surface inhomogeneity, original or obtained during the manufacture of electrodes and when installing them into a working environment of electrolytic cells. This direction was proposed in [21] and implies micro-borating of inert cathodes based on refractory metals such as carbides and borides of titanium, zirconium, etc. Here the authors will present the results of one of the experiments to eliminate microdefects of a carbon cathode by forming a wettable coating based on titanium diboride on its surface.

A method for eliminating micro- and macrodefects of the surface. The key point of the proposed method is electrochemical borating of a carbon-titanium cathode, i.e. micro-borating of the surface of a carbon cathode containing titanium in metallic form and in the form of its oxides. Carbon-titanium cathodes were preliminarily prepared in laboratory conditions by mixing an initial anthracite-graphite batch with titanium additions, pressing and firing for 4 days under a layer of petroleum coke. The electrolyte for the experiment was prepared on the basis of technical cryolite with adjusting of its c.r. up to 2.5 by addition of chemically pure NaF and AlF_3. The amount of alumina and borax $Na_2B_4O_7$, in comparison with the previous experience, decreased to 4.0 and 3.0 wt.%, respectively. Any addition of calcium compounds was excluded. During 45 hours of the experiment, the current density was maintained at 0.7 A/cm^2 and every 3 hours, 0.4 wt% Al_2O_3, 0.75 wt% $Na_2B_4O_7$ and 0.5 wt% AlF_3 were dosed. The analysis and identification of the processes occurring at the cathode were carried out in accordance with the known technique[1].

The dynamics of the voltage at the beginning of the experiment confirms an intensive formation of complexes that dissolve in the electrolyte as the melt is depleted in electroactive components (fig. 6).

Table 2. Experimental parameters and composition of precipitates of samples (XRD data)
Таблица 2. Параметры эксперимента и состав осадка образцов (данные рентгенофазового анализа)

Parameters and composition		No. of experiment		
		1	2	3
Original composition of electrolyte, wt.%	c.r.	2.7	2.7	2.5
	Al_2O_3	8.3	5	5
	$Na_2B_4O_7$	12.7	8.9	5
	CaF_2	4.6	–	–
Time of experiment, h		24	22	24
Voltage, V		~ 2.48	~ 2.82	~ 3.0
Current density, A/cm^2		0.4	0.4	0.7
Phase name	**Sampling point**	**Content, wt.%**		
Al	cathode surface	0	0	10.0
Al_4C_3	cathode surface	0	0	17.2
Al_2O_3	cathode surface	–	0	5.03
	precipitate		4.71	3.3
CaB_6	cathode surface	15.4	4.26	0.66
	precipitate	12.3	3.6	5.14
Na_3AlF_6	cathode surface	23.3	27.7	34.6
	precipitate	75.3	58	67.3
$Na_5Al_3F_{14}$	cathode surface	–	17.8	–
	precipitate	–	31.3	5.26
NaF	cathode surface	0	0	7.6
	precipitate	8.8	0	0.7
C (graphite)	cathode surface	33.1	34.6	23.7
	precipitate	1.7	0.52	0.71
Crystalline phase	cathode surface	20÷25	6.44	–
	precipitate	0	–	–
Amorphous phase	cathode surface	10	–	–
	precipitate	15÷20	–	–

For the first 9 h, boron was successively reduced from compounds with the lowest decomposition potentials. The initial voltage was stepped down to the sites at 2.600 and 2.450 V, where borax and boron oxide were reduced. After this period of limited dosage of aluminum and boron oxides in the electrolyte, electropositive ions in the melt were consumed, and the voltage rose sharply to discharge potentials $Al_4B_2O_9$ ~ 2.810 V (see fig. 6). In this mode of reduction of boron complex compounds on a carbon-titanium cathode, the process lasted 17 h accompanied by reactions of boron interaction with the components of the substrate:

$$4B + C = B_4C,$$
$$\Delta G^0_R = -58.10 \text{ kJ};$$

$$Ti + 2B = TiB_2,$$
$$\Delta G^0_R = -303.00 \text{ kJ};$$

$$3Ti + B_4C = 2TiB_2 + TiC,$$
$$\Delta G_R^\circ = -557.50 \text{ kJ}.$$

These reactions give depolarizing effects into the general process, which are depicted on the graph in the form of voltage fluctuations around the level of 2.810 V. Moreover, since the electrolyte with boron oxide dissolved therein is

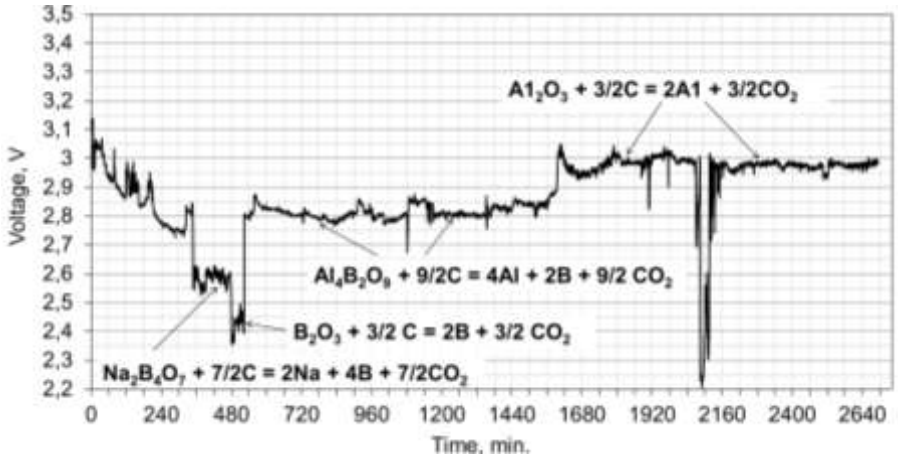

Fig. 6. Dynamics of voltage for the experiment
Рис. 6. Динамика напряжения эксперимента

freely accessible, the following reactions are quite likely:

$$B_2O_3 + Ti + 3/2C \rightarrow TiB_2 + 3/2CO_2,$$
$$\Delta G_{1300K} = -322.20\ kJ;$$

$$B_2O_3 + TiO_2 + 5/2C \rightarrow TiB_2 + 5/2CO_2,$$
$$\Delta G_{1300K} = -365.97\ kJ.$$

After exhaustion of boron ions, electrolysis continued at a voltage of 2.980 V by the electroreduction of $Al^{3+}+3e \rightarrow Al$ to metallic aluminum. The wetting properties of the substrate ensured the presence of an aluminum layer on the cathode surface (fig. 7). Good adhesion of the metal to the cathode did not permit sampling the surface for XRD analysis.

Thus, at 980°C and 0.7 A/cm^2, conditions were created under which, during the first 26 h of the experiment, the borating of the carbon-titanium surface occurred. The sources of boron in this case were successively the processes of electrochemical decomposition of B_2O_3 and its oxide complexes $Al_4B_2O_9$, $Na_2B_4O_7$, $Al_4B_2O_9$. After the boron was consumed, the voltage of the electrolysis process increased until the alumina decomposed, and an aluminum layer appeared on the cathode surface with good adhesion to the surface.

When exposed to a damp atmosphere, the carbon sample was destroyed. Therefore, SEM-EDS analysis was carried out on the areas of the completely saved surface of the boundary between aluminum and carbon, from the back side, inaccessible before (fig. 8). Note that upon a closer view, destruction occurred along the sample body, but not along the aluminum-carbon boundary. This directly confirms the complete adhesion and wetting of aluminum on the cathode surface.

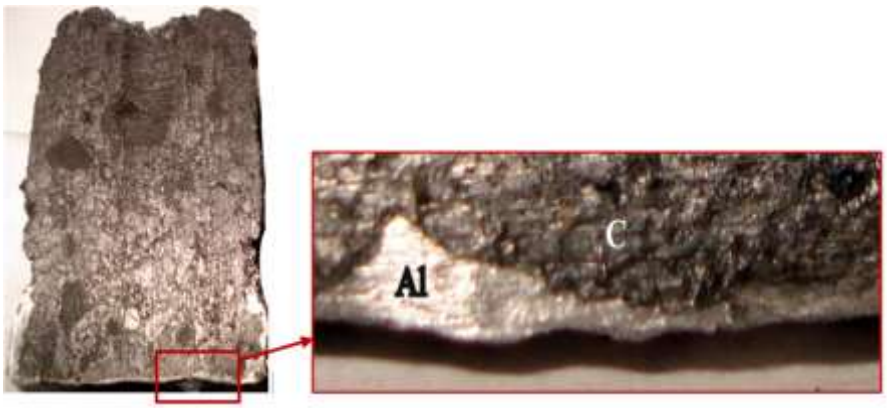

Fig. 7. Appearance of the cathode after the experiment
Рис. 7. Внешний вид катода после опыта

Fig. 8. Aluminum layer and its inner surface
Рис. 8. Слой алюминия и его внутренняя поверхность

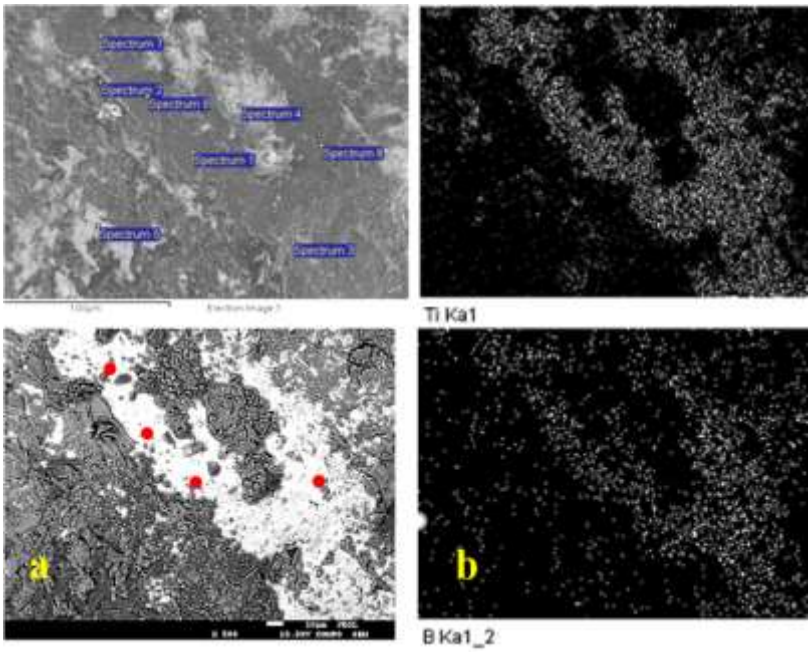

Fig. 9. The microstructure of the sample (×500): a – SEM analysis; b – EDS maps of Ti and B
Рис. 9. Микроструктура образца (×500): a – SEM-анализ; b – EDS-карты Ti и B

The back surface was cleaned according to a standard technique, mechanically and using diamond suspensions. However, complete cleaning of the cathode surface from carbon particles, without removing the layer under them, is impossible. Therefore, when viewing an image in compositional contrast, a dark-coloured field is a relief mixture of the remnant of carbon particles directly adjacent from above to the bright field (located below, between the aluminum layer and the carbon surface, see fig. 9 *a*). This bright field, as shown by the EDS analysis, is a layer of boride compounds created during a 45-hour experiment. When examining the data of energy-dispersive mapping of this area, the complete and concentrated coincidence of the boron and titanium fields is visually easily detected (fig. 9 *b*). The marked points 1 and 6–8 belong to the TiB_x layer adjacent directly to the aluminum (tab. 3). There are also minor electrolyte impurities.

Table 3. Results of energy-dispersive analysis
Таблица 3. Результаты энергодисперсионного анализа

Points in fig. 9 *a*	Linear spectra of the sample, at.%, ×500									TixBy
	B	Ti	C	O	F	Na	Al	Si	Ca	
1	62.28	32.09	–	–	4.21	0.39	1.03	–	–	$TiB_{1.94}$
6	74.42	23.26	–	–	1.54	0.31	0.46	–	–	$TiB_{3.2}$
7	59.87	31.44	–	–	4.48	0.89	1.92	1.40		$TiB_{1.9}$
8	66.22	28.68	–	–	2.38	0.57	2.15	–	–	$TiB_{2.3}$

Thus, one can state that the well-observed wetting of the cathode surface with aluminum is due to the TiB_2 layer, and this titanium diboride layer was formed on a polycrystalline carbon electrode, the initial surface of which had a high degree of micro- and macro-defects. It can be assumed that by a similar mechanism, the surface microdefects of inert electrodes will be eliminated by boron reduction in initial and obtained impurities in the form of oxides, oxycarbides, and borates of the main cathode material:

$$2B + Ti = TiB_2,$$
$$\Delta G^0_{1300} = -320 \text{ kJ/mole};$$

$$3B + TiBO_3 = TiB_2 + B_2O_3,$$
$$\Delta G^0_{1300} = -228 \text{ kJ/mole};$$

$$4B + TiO_2 = TiB_2 + B_2O_2\uparrow,$$
$$\Delta G^0_{1300} = -119 \text{ kJ/mole};$$

$$2B + TiC_{0.5}O_{0.5} \rightarrow TiB_2 + 1/2CO,$$
$$\Delta G^0_{1300} = -81 \text{ kJ/mole}.$$

This process (micro-borating of the cathode surface) must be carried out continuously throughout the entire life of the cell, since the cathode surface is subject to constant oxidation by dissolved and gaseous anode gases.

CONCLUSION

On the basis of the conducted laboratory research into the passivation mechanism of polycrystalline cathodes, a method for carrying out stable electrolysis using solid electrodes is presented.

The performed complex analysis of electrolysis conditions, the appearance of the initial and spent carbon cathodes, as well as the data of XRD analysis and electron-microscopic studies showed that a dense layer of precipitates on the cathode is formed due to micro- and macrodefects of the electrode surface.

Under the standard conditions of the diffusion control of the cathode process, a discharge of aluminum ions occurs on a homogenous surface of liquid aluminum. The concentration polarization of this process and an increase in current density to the limiting values take place only provided the deficiency of potential determining ions, associated with a decrease in the alumina concentration to critical values.

When using composite cathodes, which are inevitably characterized by micro- and macrodefects, the process leads – gradually or in an avalanche manner – to growing current concentrations and current densities on protrusions, ribs, pore edges, scratches, cold shuts and other defects. As the process accelerates, concentration polarization develops successively, with a deficiency in complex ions of aluminum, mixtures and electrolyte components. Under these conditions, an *n*-layered precipitate of impurities and electrolyte components is also gradually formed on the cathode. The results of these processes are obvious, i.e. the passivation of the cathode and an overall imbalance of the electrolysis.

The discussed mechanism of passivation of the carbon cathode as a polycrystalline product can be applied to all composite electrodes, including those based on titanium diboride.

A logical way to overcome these limitations is to eliminate the surface heterogeneity, either original or resulting from the processes of electrode manufacture and installation into the operating environment of electrolytic cells.

In this regard, a possible approach to reducing the surface heterogeneity at the micro- and macrolevel is micro-borating of the metal-containing cathode. The conducted SEM-EDS analysis revealed that, during a laboratory experiment at 980°C and under a current density

of 0.7 A/cm^2, the inhomogeneous cathode surface was homogenized with a titanium diboride layer. An aluminum layer was electrodeposited on the cathode at stable electrolysis parameters.

The presented results and analysis of the laboratory study of electrolysis using solid electrolytes, with a focus on the features of their polycrystalline structure and taking into account the chemical and physical inhomogeneity, are only the first steps in this direction.

Therefore, it is necessary to continue the research using special techniques and specific conditions of electrolysis. At the same time, or rather in parallel with laboratory experiments, the development of theoretical grounds is required to elucidate and overcome the limitations of electrolysis using solid electrodes. The following part of the present paper will contribute to the theory and theoretical calculations of the electric field distribution on an inhomogeneous surface taking into account the edge effects of current concentrations on the electrodes.

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