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## Development and Industrial Tests of the TiB<sub>2</sub>-Based Composite Material for Local Fractures Repairing of Electrolyzer Bottom Blocks

**G. E. Nagibin<sup>a, \*</sup>, A. V. Zavadyak<sup>b, \*\*</sup>, I. I. Puzanov<sup>b, \*\*\*</sup>, A. V. Proshkin<sup>b, \*\*\*\*</sup>,  
E. N. Fedorova<sup>a, c, \*\*\*\*\*</sup>, S. S. Dobrosmyslov<sup>a, c, \*\*\*\*\*</sup>,  
I. A. Kirillova<sup>a, \*\*\*\*\*</sup>, and N. V. Sukhodoeva<sup>d, \*\*\*\*\*</sup>**

<sup>a</sup>*Siberian Federal University, Krasnoyarsk, 660041 Russia*

<sup>b</sup>*OOO RUSAL Engineering-and-Technological Centre, Krasnoyarsk, 660067 Russia*

<sup>c</sup>*Institute of Computational Technologies SB RAS, Krasnoyarsk Branch Office,  
Krasnoyarsk, 660049 Russia*

<sup>d</sup>*Federal Research Centre Krasnoyarsk Scientific Centre, Siberian Branch, Russian Academy of Sciences,  
Krasnoyarsk, 660036 Russia*

\**e-mail: Nagibin1@gmail.com*

\*\**e-mail: Andrey.Zavadyak@rusal.com*

\*\*\**e-mail: Iliya.Puzanov@rusal.com*

\*\*\*\**e-mail: Aleksandr.Proshkin@rusal.com*

\*\*\*\*\**e-mail: Efedorova@sfu-kras.ru*

\*\*\*\*\**e-mail: Dobrosmyslov.s.s@gmail.com*

\*\*\*\*\**e-mail: Iakirillova17@gmail.com*

\*\*\*\*\**e-mail: Suhodoevanadezda@gmail.com*

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**Abstract**—The composition and fabrication technology of a repair mixture consisting of unmolded corundum with a TiB<sub>2</sub>-C composite coating wettable with aluminum for repairing local fractures of bottom blocks without interrupting electrolysis have been developed. The proposed technical solution makes it possible to decrease the bottom wear and prolong the service life of an aluminum electrolyzer by six months. To fabricate a repair mixture with an optimal composition, the titanium diboride powder with a refractory powderlike binder in ratio 50 : 50 (wt %) is used. Unmolded corundum is coated with this mixture of a binder and titanium diboride. This material is dried at 150°C and thermally treated in a carbon bed at  $t = 700\text{--}900^\circ\text{C}$ . Calcination in a reducing gas atmosphere results in the formation of the TiB<sub>2</sub>-C composite material with a carbon content of 15–20 wt % on the unmolded corundum surface. The qualitative evaluation of the properties of the developed composite coating shows that it has rather high hardness, wear resistance, and adhesion to the base after calcination. To perform pilot tests, the repair mixture is poured with molten aluminum, which gives the platelike repair mass of the Al-TiB<sub>2</sub>-C composition. Pilot tests of the repair mass using an RA-400 operating electrolyzer at the pilot shop of OAO RUSAL-Sayanogorsk show that the bottom wear decreases within three months after the repair of the local fracture with uninterrupted electrolysis. This fact is evidenced by a 13% decrease in an average fracture depth with a stable current force of 4.7–4.8 kA/bloom after the repair. Thus, the local use of the repair mass retards the overall wear of the cathodic surface and makes it possible to prolong the service life of the electrolyzer.

**Keywords:** aluminum electrolyzer, bottom block, local repair, titanium diboride, composite coating, wear

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### INTRODUCTION

The development of efficient environmentally safe technologies is an urgent task of aluminum industry, along with an increase in electrolyzer power [1, 2]. An increase in the ampere loading and cathodic current density, which is characteristic of high-ampere elec-

trolyzers with calcined anodes of RA-400 and RA-550 type, leads to a change in the kinetics of the physico-chemical interaction of cryolite–alumina melt with a carbon-graphite bottom [3]. A cathodic bottom is one of the most vulnerable constructional elements of the electrolyzer, which determine its service life. The surface of the graphite carbon cathode is subjected to

continuous wear with a rate from 10 to 30 mm/yr and larger; herewith, the wear rate increases with the enhancement of the current force and an increase in the degree of graphitization [1, 4].

The wear of the bottom block proceeds most intensely in high-density regions—in the side lining zone immediately above blooms. The middle of the bottom block is subjected to erosion to a lesser extent. Thus, the wear (erosion) profile of the bottom tends to a *W*-like shape [1, 5].

The erosion of cathodic blocks is reason for the premature mortality of the electrolyzer. As a rule, the replacement of the cathodic bottom (complete or partial) requires electrolyzer switching-off, pouring metal and electrolyte, dismantling the anodic facility, and the removal of residues of solidified metal and electrolyte from the bath with the subsequent removal of the worn coal lining [6]. To reconstruct the worn bottom, certain cathodic blocks are replaced either by new ones or by one block to the entire bottom depth from a nonconductive material, for example, vinyl resin [7–11]. One disadvantage of this method is the total stoppage and electrolyzer startup, like after an overhaul. In addition, bottom integrity is not provided, which requires temporary protection for the place that has been repaired and additional service costs.

A collective of authors [12] proposed a repair method for the lining without switching off the electrolyzer, which includes preliminary cleaning of fractured places and their push fit by a mass consisting of a mixture of magnesite powder and aluminum. A mixture is sequentially deposited layer-by-layer. This procedure makes it possible to form a composite material with a high wear resistance and electrical conductivity due to the addition of  $MgCO_3$  and impregnation by liquid aluminum.

There are alternative repair methods that make switching off the electrolyzer unnecessary, in which inhomogeneous bottom wear is taken into account. To retard its fracture process, places of the maximal wear are poured by mixtures of various compositions, in particular, by breakage wastes of silicon carbide blocks, periclase powders with various granulometric compositions, or a mixture formed due to the fusion of fluorine-containing salts ( $AlF_3$  and  $CaF_2$ ) of electrolytic aluminum production [3]. The bottom integrity is violated when using such repair methods, and resistivity in repair places exceed 10–40  $\mu\Omega$  cm (depending on the degree of graphitization). This results in the redistribution of the current and the degree of the wear increases for other bottom areas. Disadvantages of the listed methods include the application of materials nonwettable by aluminum and the necessity of using high temperatures to alloy the components, which lowers the economical efficiency of the repair.

The main idea of the technical solution proposed in our work is to develop conductive repair material with a high wear resistance with a low repair prime

cost. This idea can be implemented when using components wettable by aluminum and substantially increasing the functional properties of the material. The most promising Al-wettable substance—the base of the repair material—is titanium diboride ( $TiB_2$ ) as a heatproof material possessing high hardness, low electrical resistance, chemical stability in liquid aluminum, and thermal-shock resistance [13–17]. The application of composite coatings with the  $TiB_2$ -C composition promotes the formation of numerous conducting veins in the bulk of the material filling damaged places, which makes it possible to retain the current distribution over the blooms and prevent the further local wear of bottom blocks [18, 19].

Thus, our study is aimed at developing the composition of the  $TiB_2$ -based repair material with the composite coating and the repair method of local bottom fractures with uninterrupted electrolysis. This technical solution will make it possible to decrease the wear of the cathodic surface and prolong its service life.

## EXPERIMENTAL

The initial components for the formation of the repair mixture were as follows: corundum (*TU* (Technical Specifications) 3988-012-00658716–2002, produced by AO RUSAL Boksitogorsk), RA-2 powder of titanium diboride (*TU* 6-09-03–75, produced by OAO UNIKHIM s OZ, Yekaterinburg), and production additive—a refractory binder produced by OAO Poliplast-UralSib, Pervoural'sk, which represents the sulfated products of the interaction reaction of naphthalene with formaldehyde with a coke residue no smaller than 15 wt % (*TU* 5746-062-58042865–2011).

The granulometric composition of initial  $TiB_2$  powders was determined using an Analysette 22 MicroTec plus laser device for measuring the particle size (Fritsch, Germany) according to the ISO 13320:2009 procedure. The qualitative analysis of crystalline phases of initial powders of titanium diboride by the X-ray phase analysis (XPA) was performed using a D8 Advance X-ray diffractometer (Bruker, Germany) with the application of  $CuK_\alpha$  radiation ( $\lambda = 0.15406 \text{ \AA}$ ), recording range  $2\theta = 10^\circ - 75^\circ$  with a step of  $0.07^\circ$ . The X-ray spectra analysis (XSA) of the samples was performed using an XRF-1800 automated wave X-ray fluorescent spectrometer (Shimadzu, Japan) with a Rh anode. The surface morphology, shape, and size of  $TiB_2$  powder particles were studied using a JSM 6490-LV scanning electron microscope (SEM) (JEOL, Japan). The hardness and adhesion strength of the  $TiB_2$ -based composite coating were determined upon the deposition of the material on a corundum substrate using a TH-130 dynamic hardness meter (China) and during tensile tests (according to ISO 4624:2002) of specially prepared samples using an Instron 3369 universal testing machine (Great Britain). The resistivity of the

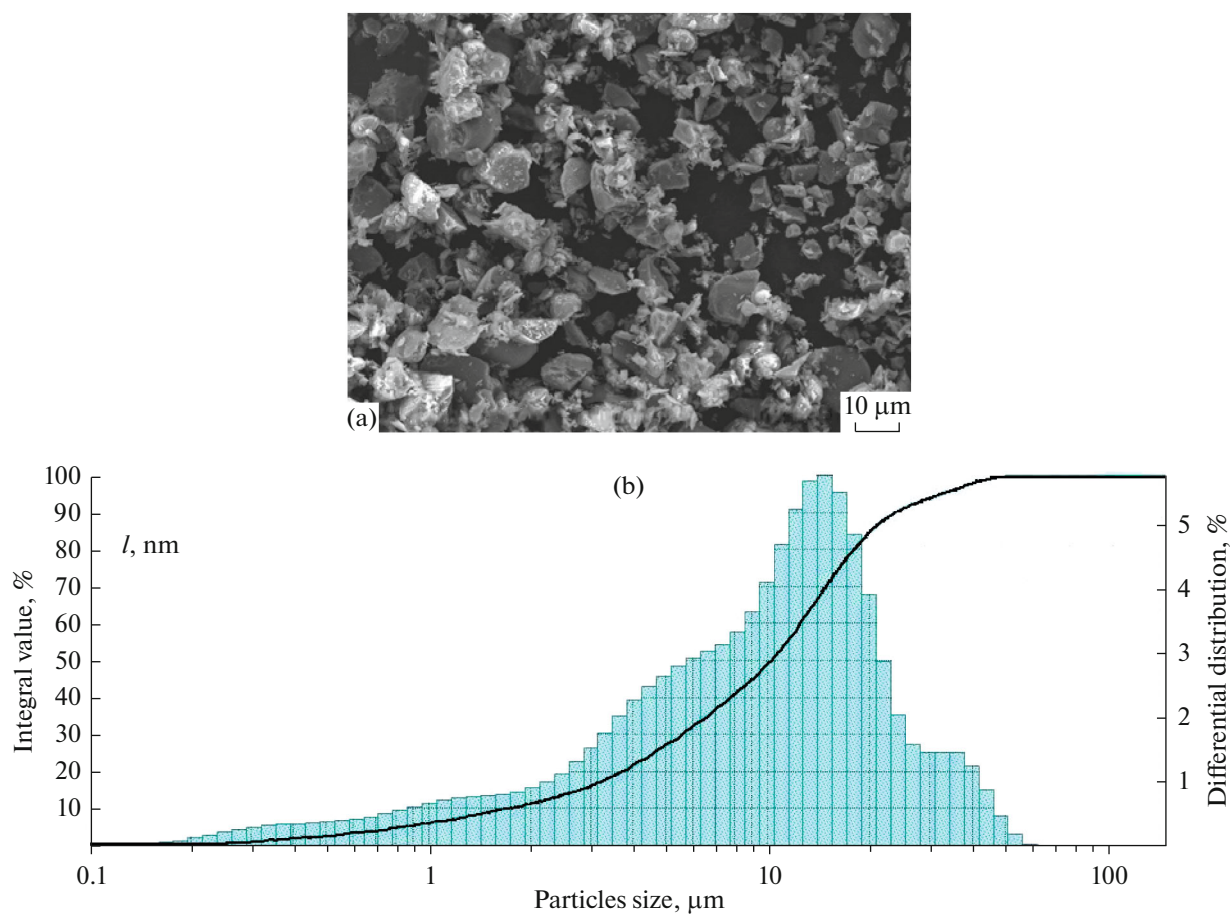


Fig. 1. (a) SEM microphotograph and (b) results of the granulometric analysis of initial  $\text{TiB}_2$  powder.

composite material was measured using a four-probe method (*GOST* (State Standard) 23776-79).

When performing pilot tests of the repair mixture, the mass fraction of titanium in aluminum was monitored in conditions of a pilot area of OAO RUSAL Sayanogorsk using an ARL3560 optical emission spectrometer (ThermoARL, Switzerland) according to *STP-4.82.12-2012* (Enterprise Standard) "Primary and Deformable Aluminum. The Method of Optical Atomic-Emission Spectrometry of Determining Mass Fractions of Impurities." The control of the current distribution over blooms was performed according to

the procedures acting at OAO RUSAL Sayanogorsk using an IPT 2010 direct current meter (ZAO Kraspromavtomatika, Krasnoyarsk).

Characteristics of the initial components of the repair mixture are presented in Table 1.

Figure 1 shows a microphotograph of initial titanium diboride powder and results of granulometric analysis.

The  $\text{TiB}_2$  powder is characterized by a platelet particle shape; the average particle size is 10  $\mu\text{m}$ . The apparent and true densities of the powder are 1.3 and 4.1  $\text{g}/\text{cm}^3$ , respectively.

Table 1. Characteristics of initial materials

Material	Chemical composition, wt %			Physical properties	
				apparent density, $\text{g}/\text{cm}^3$	granulometric composition, mm
Titanium diboride	$\text{TiB}_2$	Mg	Fe	2.5	0–0.1
	>98	≤0.1	≤0.1		
Corundum	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{NaO}_2$	1.7	1–10
	95.5	0.1	0.4		

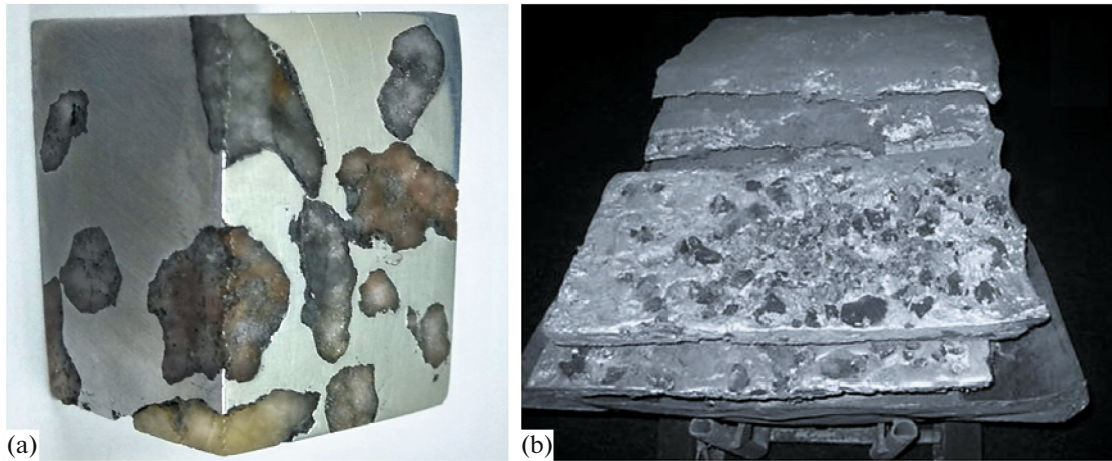


Fig. 2. (a) Cuts of the composite after pouring with molten aluminum and (b) repair mass in the form of plates for pilot tests.

### FABRICATION METHOD OF THE REPAIR MIXTURE

To fabricate the repair mixture,  $\text{TiB}_2$  powder was mixed with an aqueous solution of a fireproof powder-like binder until a homogeneous mass was formed. Then unmolded corundum was coated with this mixture and dried at  $t = 150^\circ\text{C}$ . The material was roasted in a carbon filler in a fireproof steel container in a PVK 1.4-36 laboratory chamber furnace at  $t = 700\text{--}900^\circ\text{C}$ . The necessity of using the reducing atmosphere is conditioned by the active oxidation of  $\text{TiB}_2$  at temperatures above  $800^\circ\text{C}$ .

According to [20], the carbon additive during the decomposition of thermoplast applied as a fireproof binder makes it possible to increase the electrical conductivity of the  $\text{TiB}_2$ -based composite coating by  $\sim 10\%$ . However, exceeding the critical binder concentration leads to the loss of the material wettability by aluminum and an increase in the material shrinkage due to the removal of volatile decomposition products. In connection with this fact, we studied the selection of optimal compositions of a composite coating. Finally, it is established that the critical binder concentration is 70%. Exceeding the mentioned value leads to coating bulging in the course of drying and subsequent calcination.

Another important process parameter is composition viscosity. It was revealed experimentally that it should be in limits of  $400\text{--}700\text{ mPa}\cdot\text{s}$ . The composition deposition on unmolded corundum at higher viscosity by a smooth layer is complicated. The mentioned viscosity range corresponds to the composition (wt %)  $50\text{TiB}_2\text{--}50$  binder.

Calcination in the reducing medium results in a  $\text{TiB}_2\text{--C}$  composite material with a carbon content of 15 wt %, which was determined by the XSA method, being formed on the surface of unmolded corundum. To increase the analysis accuracy, we also determined the carbon content in the samples using the gravimet-

ric method by weight loss during calcination (in air at  $t = 800^\circ\text{C}$  for 2 h).

It should be noted that this composition ( $85\text{TiB}_2\text{--}15\text{C}$ , wt %) satisfies the economical requirements, because the partial replacement of high-cost  $\text{TiB}_2$  by carbon lowers the prime cost of the material used for the repair of local fractures of bottom blocks [21, 22].

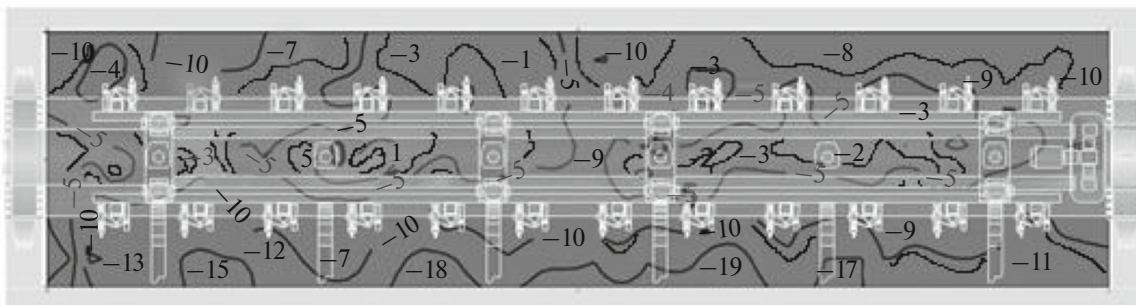
To evaluate wettability with aluminum of the composite coating material, we fabricated castings (Fig. 2a), which were prepared by the immersion of unmolded corundum with the  $\text{TiB}_2\text{--C}$  coating into molten aluminum ( $t = 800^\circ\text{C}$ ).

The hardness of the composite coating was  $327 \pm 10\text{ HB}$ , the adhesion strength was 2.4 MPa, and resistivity was  $35\text{--}70\ \mu\Omega\text{ m}$ .

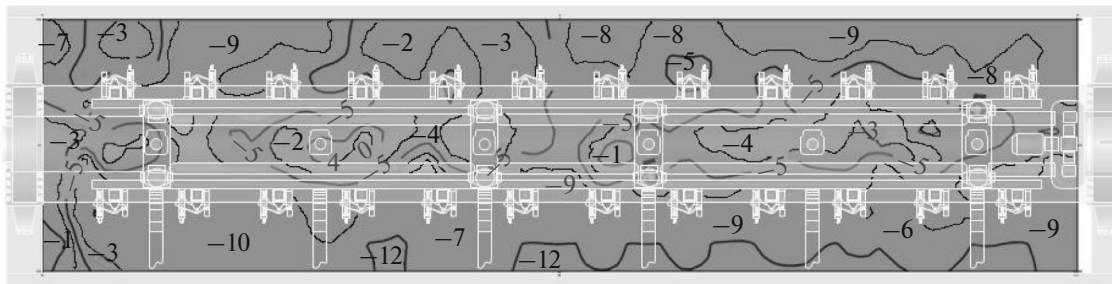
The sequence of manufacturing operations for the formation of the repair material (the formation of the repair mixture of  $\text{TiB}_2$  powder and a binder, coating of unmolded corundum with this mixture, coating drying and calcination, and immersion of unmolded corundum with the  $\text{TiB}_2\text{--C}$  coating into molten aluminum) implemented under laboratory conditions was used to perform pilot tests during the local repair of bottom blocks of an RA-400 operating electrolyzer at the pilot shop of OAO RUSAL-Sayanogorsk. After pouring the repair mixture, which is unmolded corundum with a  $\text{TiB}_2\text{--C}$  coating, by molten aluminum, we acquired a platelike mass (Fig. 2b).

### PILOT TESTS OF THE REPAIR MIXTURE

The repair of local fractures of the cathodic bottom was performed with uninterrupted electrolysis. We investigated the topography of the cathodic surface to determine the location and depth of damages (cavities). Topographic measurements were performed by probe immersion into the melt of electrolyte and liquid aluminum in various points over the entire



**Fig. 3.** Topographic map of the bottom fracture of the RA-400 electrolyzer relative to the initial state (the service life is 55 months; digits denote the degree of the wear depth, %).



**Fig. 4.** Topographic map of the bottom of the RA-400 electrolyzer three months after the local repair (service life is 58 months; digits denote the degree of wear depth, %).

cathodic surface. The topographic map of the electrolyzer bottom wear with a service life of 55 months is presented in Fig. 3.

According to the data of our measurements, the average cavity depth is 6.8 cm (Table 2). Areas were established where the wear occurred almost threefold more intensely. These were the areas where the local repair was performed. Cavities were filled by the plates of the preliminarily prepared repair mass (Fig. 2b). The immersion direction was specified using metallic rods arranged over the cavity boundaries.

The local repair was accompanied by monitoring of the bottom state during the operation. The tests of the repair mass were performed for three months. To do this, regular sampling of metal specimens was per-

formed, and they were analyzed for impurity content by optical atomic emission spectroscopy. The process measurements allowed us to monitor the electrolyzer operational mode, including the current distribution over blooms. Topographic measurements were also repeated after the local repair over the bottom surface.

Figure 4 shows the topographic map of the bottom surface of the RA-400 electrolyzer three months after the repair of local bottom fractures. When compared to Figs. 3 and 4, it is seen that we succeeded in retarding the bottom wear due to local repair using the developed composite material.

Table 2 shows the damage depths of the cathodic area relative to the initial state and the current distribution over the blooms of the RA-400 electrolyzer

**Table 2.** Comparative damage depths of the cathodic area relative to the initial state and current distribution over the RA-400 electrolyzer blooms before and after the repair of local bottom fractures

Performance of measurements	Average value	Mode	RMS	Max	Min
Damage depth, cm					
Before repair	-6.8	-5	3.86	-18	5
Three months after repair	-5.9	-8	2.88	-10	4
$\Delta$	$\downarrow 0.9$	$\uparrow -3$	$\downarrow -0.98$	$\downarrow 8$	$\downarrow -1$
Current force, kA/bloom					
Before repair	4.79	5.3	0.79	3	6.1
Three months after repair	4.75	5.5	0.75	3	6
$\Delta$	-0.04	0.2	-0.04	0	-0.1

RMS is the root-mean-square deviation,  $\Delta$  is the variation of the quantity after the local repair, and  $\downarrow/\uparrow$  is decrease/increase of values.

before and after the repair of local bottom fractures. It is seen that an average damage depth decreased at a stable current force (4.75 kA/bloom). Despite the fact that the mode magnitude increased, i.e., the total bottom wear continues, the fracture of most vulnerable cathode areas retarded after the local repair. This fact is evidenced by a decrease in an average damage depth upon a stable current force.

According to its state upon measurement after the repair, the age of the RA-400 experimental electrolyzer was 58 months; no bottom fracture or violation of the current distribution over the blooms was observed.

## CONCLUSIONS

Our investigations resulted in the development of the composition and fabrication technology of a material consisting of unmolded corundum with the  $TiB_2$ -C composite coating wettable by aluminum for the repair of local fractures of bottom blocks with uninterrupted electrolysis.

Pilot tests confirm the efficiency of the proposed technical solution. The investigations of the bottom topography before and after repair showed that the local use of the repair mass retarded the wear of the cathodic surface and made it possible to prolong the electrolyzer service life by six months.

## FUNDING

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## CONFLICT OF INTEREST

The authors claim that they have no conflict of interest.

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