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Low-temperature Synthesis of Composite C-TiB_2 Electrodes in Standard Firing Processes and in Molten Salt Electrolysis

E. S. Gorlanov, G. G. Popov*, T. N. Kopylova, A. S. Gontsukov, O. A. Mozulev

Saint Petersburg Mining University, Saint Petersburg, Russia

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A B S T R A C T

In the article the results of laboratory investigations of two versions of low-temperature synthesis for compact composite carbon - titanium carbide/titanium diboride (C – TiC/TiB_2) are presented. The article concerns the preliminary examination of the thermodynamic probability of titanium carbide and titanium boride synthesis during the process of standard baking at the temperature of 1050±10ºC in the volume of carbon electrode, which composition contains boron oxide and one of the refractory metals; the synthesis taking place directly during the electrolytic reduction of the melts at the temperature of 965-970°C in the volume of carbon cathode, containing metal oxides, is also examined. After preliminary standard preparation of mixing the initial components (petroleum coke, metallic titanium Ti, titanium oxide TiO_2, boron oxide B_2O_3 and binder), cathode samples were formed, which were calcined under a layer of petroleum coke. Experiments with different holding times during the electrolytic process showed a continuous film of aluminum on the surface of the cathode, which indicates acceptable wettability. The presence of TiC/TiB_2 was confirmed by X-ray phase analysis and X-ray structural analysis (SEM-EDS analysis). Innovative technologies presented for the production of composite electrode materials could be used for the synthesis of wide range of the composite products in C – MeC/MeB_2 system. The equivalent value of petroleum coke and oxides of refractory metals allows supposing the short payback period of the use composite cathode blocks in existing pots and in pots under design.

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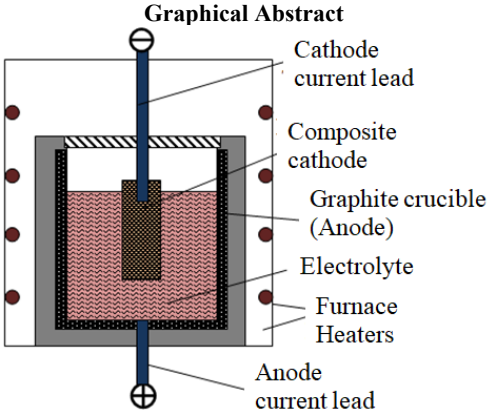
Graphical Abstract



NOMENCLATURE

ΔG	The Gibbs free energy change	E	*Electrode potential*

*Corresponding Author Email: popov_gg@pers.spmi.ru (G. G. Popov)

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1. INTRODUCTION

Main directions of the technology development in modern industry are production of more marginal products (1, 2), modernization of existing technological processes (3), increase of the depth of waste processing (4), decrease of pollutant emissions, whether that be waste effluents (5) or decarbonization processes of emissions from industrial facilities (6, 7). One of the critical points is to increase the service life of the equipment through the raw material preparation (8) or through an increase in corrosion resistance of materials (9).

Carbon cathodes in aluminum electrolytic production units fail due to carbide formation and sodium penetration (10-12) and due to the abrasive wearing (13-15), even in spite of proposed methods for the surface protection. For example, any carbon materials are not wetted by liquid aluminum without additional processing; which stimulates destructive processes (16, 17) and restrains development of new innovative technologies. To reduce negative consequences of these processes it is proposed to use electrochemical coatings from refractory compounds (18) and/or adhesion pastes, based on titanium diboride TiB_2 (19-21). These technical solutions shall improve working properties of cathode blocks, but for the limited initial time period, after which the coatings will peel off and collapse due to thermal expansion. The solution of these problems is found in the use of refractory cathode structures or gradient compositions in surface layers of cathode blocks, the structural components of which are *TiC* and *TiB_2* (22). The monography and the overview (23) contain the detailed consideration and discussion of these directions that took place from 1930-s to 2022. In most cases researchers confirm the efficiency of the electrode protection by refractory compounds in laboratory conditions or in pilot tests on industrial sites. However, none of world corporative scientific research centers could solve these problems completely and finally. Available alternatives are not widely accepted or are not used in the metallurgical industry. According to the authors, a promising direction for the creation of corrosion-resistant and aluminum-wettable materials is the use of carbon-based composite electrodes, the creation of which is carried out directly during their production or operation.

The purpose of this work is to develop the technology for the synthesis of composite electrode material, having improved working properties in conditions of standard baking of the products or during the electrolytic reduction of molten salts.

2. SUBSTANTIATION

To produce a stable composite material in aggressive environment, it requires not mechanical mixing of the carbon-containing base with alloying additives, but the interaction between them within – the intergranular space of a dense product. Refractory metals or their oxides can act as initial alloying phases with consequent conversion into corrosion-resistant compounds. This interaction between components is arranged using standard methods at high temperatures or in special conditions under low temperatures. Two options are possible to create conditions for the low-temperature synthesis of refractory compounds in C-Ti-B-O system:

1) Synthesis during the standard baking process at the temperature of 1050±10ºC in the volume of the electrode, which composition contains boron oxide and one of the refractory metals.

For example, the synthesis of titanium carbides and titanium borides could take place thermodynamically in the volume of the carbon electrode at the temperatures of 1000-1100°C (Equations 1-3):

	ΔG^0_{1300}, kJ/mol	
$2Ti+B_2O_3+4C \rightarrow TiB_2+TiC+3CO$	– 215,63	(1)
$Ti + C = TiC$	–113,44	(2)
$Ti + B_2O_3 + 3C \rightarrow TiB_2 + 3CO$	–41,13	(3)

Carbon base with alloying elements introduced into the grain boundaries modifies the operational properties of carbon-graphite products; it is quite likely that these modified products will acquire high erosion and oxidation resistance in aggressive environments.

2) Synthesis directly during the electrolytic reduction of the melts at the temperature of 965-970°C in the volume of carbon cathode which composition contains metal oxides.

This method consists in separating alloying components between the carbon cathode and electrolytic bath. For example, while introducing titanium oxide into the carbon cathode body, TiO_2 shall undergo dissolution with electrolyte filtrate. As a result, conditions are being created for the propagation of titanium within the electrode following phase boundaries of macro-structure in atomic and ionic states, in elementary form and in form of oxides (Equations 4):

$$Ti^{4+} + 4\bar{e} = Ti^0 \qquad E^0_{1300} = -0{,}807\ B \qquad (4)$$

While arranging a counter-current flow of boron from the electrolytic bath and its reduction on the surface and in the volume of the cathode the direct interaction of titanium diboride TiB_2 components takes place (Equations 5-7):

	ΔG^0_{1300}, kJ/mol	
$2B + Ti \rightarrow TiB_2$	–318	(5)

$4B + TiO_2 = TiB_2 + B_2O_2\uparrow$ –119 (6)

$2B + TiO_2 + 2C \rightarrow TiB_2 + 2CO$ –67 (7)

The interaction of new formed and active ad-atoms of titanium and boron with carbon is possible as well (Equations 8-10):

ΔG^0_{1300}, kJ/mol

$Ti + C = TiC$ –113 (8)

$4B + C = B_4C$ –58 (9)

$3Ti + B_4C = 2TiB_2 + TiC$ –-557 (10)

Thus, it is thermodynamically possible to obtain composite materials with the required corrosion and abrasion resistance. The resulting composite materials can be used as cathode blocks in aluminum electrolysis plants.

3. EXPERIMENTAL

3. 1. Preparation of Electrodes The standard procedure of mixing initial materials, their press forming and baking was used for the preparation of composite electrodes, based on C – TiB_2. The used titanium metal powder, boron oxide and rutile titanium oxide are reagents of chemical purity. Petroleum coke was obtained from LUKOIL-Permnefteorgsintez with an ash content of 0.16 wt.%. Two material compositions were preliminary prepared (see Table 1):

For composition 1, the molar ratio of titanium to boron oxide, in accordance with Equation 3, is close to stoichiometric and is approximately 1. In composition 2, the amount of titanium oxide is determined by economic considerations and the technological conditions for obtaining a compact, dense product.

Petroleum coke which particle size did not exceed 2 mm, was mixed with alloying components (Ti, B_2O_3, TiO_2) at the temperature of 115±5°C in the charge mixer during the period of 10 minutes. Then heated crushed coal tar pitch was added with thorough mixing for 15-20 minutes. The resulting plastic mass was molded into electrodes on a static press in a preheated press matrix under a pressure of ~20.0 MPa. The resulting cylindrical electrodes were covered with a layer of petroleum coke and fired in a muffle furnace (1050±20ºC).

TABLE 1. Compositions of the initial components

Initial components	Composition 1, % wt.	Composition 2, % wt.
Calcined petroleum coke	62-66	73-77
Titanium metal, Ti	8-9	-
Boron oxide, B_2O_3	13-14	-
Titanium oxide, TiO_2 (R)	-	10-12
Coal tar pitch	13-15	13-15

The synthesis of C – TiC/TiB_2 composite for composition 1 was carried out directly during the baking of specimens according to Reactions 1 to 3. The synthesis of C – TiB_2 composite for composition 2 was carried out directly during the electrolytic reduction of boron from the cryolite melt on the surface and in the volume of titanium-containing electrode (cathode) and during further Interactions 4 to 7. A total of 3 samples of composition 1 and two samples of composition 2 were prepared and tested.

3. 2. Electrolytic Reduction Process After synthesis, the electrodes were connected to the current leads of the setup using a threaded connection. The temperature in the experimental setup (see Figures 1 and 2) was set at 965-970°C in an electrolytic bath with a NaF/AlF_3 ratio of 2.4±0.1. The initial melt composition as well as the correction of the bath composition during the electrolytic process were based on the use of cryolite or chemically pure sodium and aluminium fluorides.

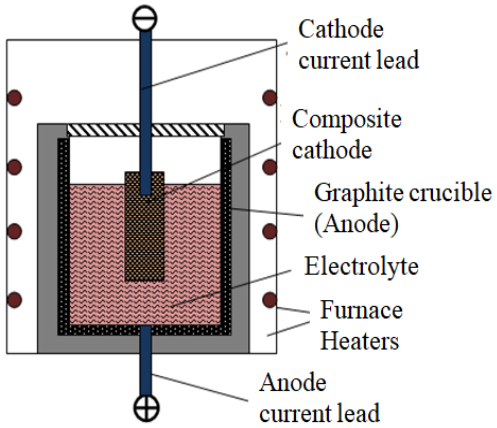


Figure 1. Cell diagram of an electrolysis cell with vertical composite electrode

Figure 2. Photo of electrolytic reduction unit in operation

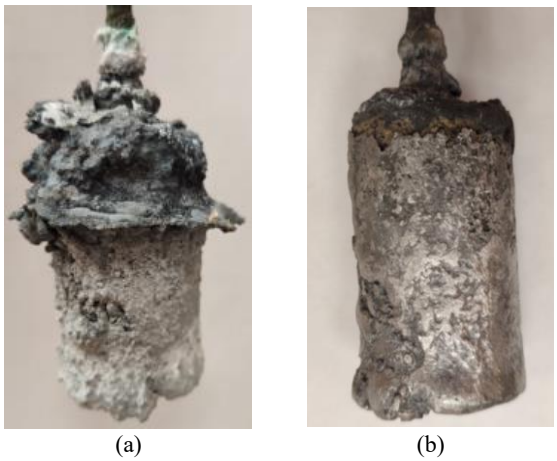
The unit turned on the reduction process with permanent registration of temperature, amperage and voltage. Experiments lasted for from 11 to 17 hours at the current density of ~0,7 A/cm^2 and voltage of 5±0,5 V. Before the end of the experiment, 4% by weight of Al_2O_3 was added to the melt to form an aluminum layer on the cathode and confirm the wettability of the composite material.

To provide the synthesis of composite of the composition 2, boron oxide (which features an unlimited solubility in cryolite melt) was introduced into the bath composition during the entire electrolytic reduction period. To establish the phase composition, the composite electrode was examined on a Shimadzu XRD-6000 analyzer. Then, on a TESCAN Vega 3 LMH electron microscope with an Oxford Instruments spectrometer, the microstructure and chemical composition (SEM-EDS analysis and EDS mapping) of the sample were studied.

4. RESULTS AND DISCUSSION

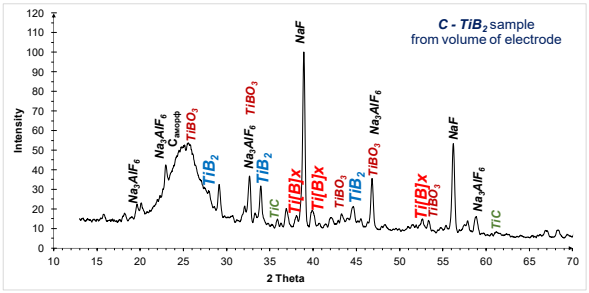
4. 1. Initial Composition 1. Electrolytic Reduction Using Prepared Composite Electrode Figure 3 shows the specimen after 11 hours of electrolytic reduction process. The surface of the electrode immersed into the electrolytic bath, is covered with continuous aluminium layer having an acceptable adhesion.

Samples were taken from the volume and from the surface layer (adjacent to the layer of aluminium) of electrodes, impregnated with electrolyte, in order to define their phase composition by method of X-ray phase analysis. Figure 4 presents X-ray patterns of the samples. In these samples, in addition to the main phase of the electrolyte group (filtrate), reflections of TiB_2, $Ti[B]_x$ borides and titanium carbide TiC are detected, pre-synthesized during the process of firing the electrodes according to Reaction 1 to 3.



(a) (b)

Figure 3. Specimen after 11 hours of electrolytic reduction a) after the electrolytic reduction process; b) after mechanical cleaning



(a)

(b)

Figure 4. Results of X-ray phase analysis of the electrode after 11 hours of electrolytic reduction process: a) sample from the volume of electrode; b) sample from the surface layer of electrode

Titanium borate ($TiBO_3$) that is present in the samples is a product of titanium diboride TiB_2 oxidation. It seems that the oxidation process takes place during the extraction of the electrode, heated to 965-970°C, out from the electrolytic cell (Equation 11):

The samples from the bulk and surface of the electrodes are practically indistinguishable in phase composition. This indicates a complete and uniform transformation of the initial components Ti, B_2O_3 and C into titanium borides and carbides during the synthesis process with standard firing of samples under a layer of petroleum coke. However, the lower intensity of the amorphous carbon peak ($C_{amorph.}$) in the sample from the surface may indicate a more complete yield of Reactions 1 to 3 involving carbon.

4. 2. Initial Composition 2. Synthesis During Electrolytic Reduction Process Figure 5 shows the electrode after 24-hour experiment, its extraction out from the melt and cleaning from the electrolyte. The surface of the cathode, which was immersed in the melt, has a continuous film of aluminum.

After exposure to air the material of electrode, impregnated with the melt, cracked. However, the layer of aluminium has not separated from the surface. This gives evidence of good adhesion and composite

(a) (b)

Figure 5. Electrode (cathode) after 24-hour experiment: a) after cleaning from electrolyte; b) 30 days after the experiment

composition of electrode, containing titanium diboride TiB2, which is confirmed by results of X-ray phase analysis (see Figure 6). It is noteworthy that in this method of synthesizing refractory compounds *in situ* directly during electrolysis, the main boride phase is a solid solution of boron in titanium $Ti[B]_x$. Probably, for complete synthesis into titanium diboride TiB_2, a longer electrolysis time is required.

In addition to the main phases that make up the electrolyte and titanium borides, reflections of titanium borate $TiBO_3$, a product of the oxidation of titanium boride according to Reaction 11, are detected.

$$4TiB_2 + 9O_2 = 4TiBO_3 + 2B_2O_3 \quad (11)$$

In the synthesis of composite materials, the scanning electron microscopy (SEM) method is one of the most important areas (24). Figure 7 examines the microstructure of the electrode surface layer – about 1 mm of surface layer, adjacent to the layer of aluminium. Results of EDS-mapping detect the presence of electrolyte filtrate, enriched with sodium fluoride NaF, and combined fields of boron and titanium.

The results of the analysis show that during the electrolytic reduction process, electrochemical and chemical processes 4 to 10 occur both on the surface and in the volume of the cathode material, the initial composition of which contains titanium oxide and boron introduced from the electrolytic bath. Thus, the carbon

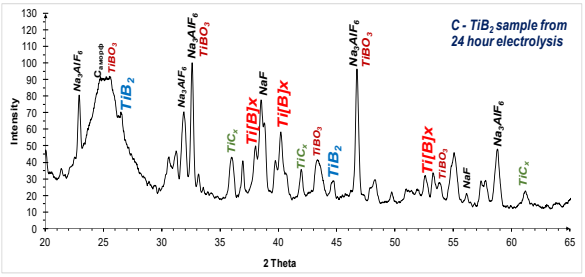
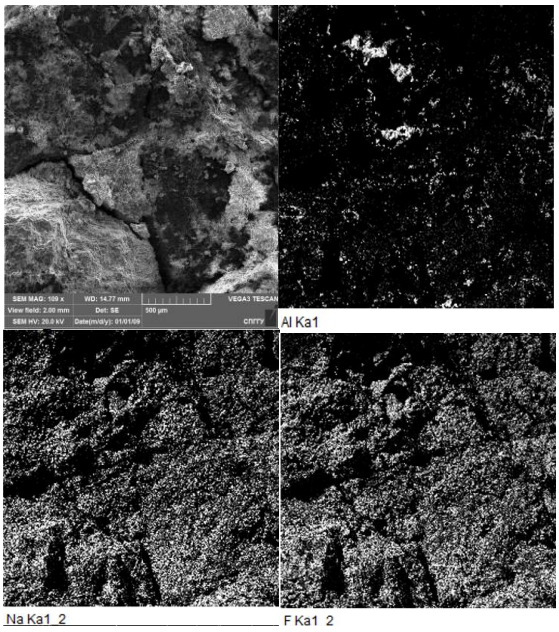
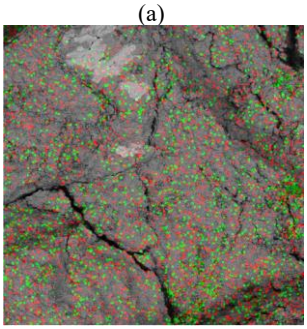


Figure 6. Results of X-ray phase analysis after 24-hour reduction process



(a)



(b)

Figure 7. SEM image electrode surfaces and EDS-mapping of electrode layer, adjacent to the layer of aluminium(scale bars and magnification levels of EDS mapping are consistent with SEM image): a) maps of electrolyte components; b) combined maps of boron (green) and titanium (red)

matrix cathode becomes alloyed with refractory compounds TiB_2 and TiC, which is a composite material. At the same time the composite cathode acquires working properties providing higher wettability in relation to aluminium and, probably, higher resistance to the abrasive wear, aggressive environment.

5. CONCLUSION

Innovative methods for the producing of composite electrode materials directly in the process of standard firing and electrolytic production of aluminum are presented. The synthesized Carbon – TiB_2 composites are wetted with aluminum and can be used both in existing and new designs of aluminum electrolyzers. Obviously, these technologies can be used to synthesize a wide range of composite products in the C – MeC/MeB_2 system.

Replacement of equivalent in cost components in the original recipe for cathode products – petroleum coke with refractory metal oxides – does not lead to a significant increase in the cost of composite products. This means that the use of the presented technology provides grounds for making a profit from the start-up period of the electrolyzer due to better metal-hearth contact, improved current distribution and stabilization of the process flow. Prerequisites for reducing the interpolar distance and increasing the current efficiency appear. In addition, the expected increased abrasive resistance of the composite hearth allows us to expect an increase in the service life of cells.

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Persian Abstract

چکیده

در این مقاله، نتایج بررسی‌های آزمایشگاهی دو نوع سنتز دمای پایین برای کامپوزیت فشرده کربن – کاربید تیتانیوم/دی‌بورید تیتانیوم ($C - TiC/TiB_2$)ارائه شده است. این مقاله به بررسی اولیه احتمال ترمودینامیکی سنتز کاربید تیتانیوم و بورید تیتانیوم در طول فرآیند پخت استاندارد در دمای ۱۰۵۰±۱۰ درجه سانتیگراد در حجم الکترود کربنی، که ترکیب آن حاوی اکسید بور و یکی از فلزات نسوز است، می‌پردازد. سنتزی که مستقیماً در طول کاهش الکترولیتی مذاب در دمای ۹۶۵–۹۷۰ درجه سانتیگراد در حجم کاتد کربنی، حاوی اکسیدهای فلزی، انجام می‌شود نیز بررسی شده است. پس از آماده‌سازی اولیه استاندارد مخلوط کردن اجزای اولیه (کک نفتی، تیتانیوم فلزی تیتانیوم، اکسید تیتانیوم TiO_2، اکسید بور B_2O_3 و چسب)، نمونه‌های کاتدی تشکیل شدند که زیر لایه‌ای از کک نفتی کلسینه شدند. آزمایش‌ها با زمان‌های نگهداری مختلف در طول فرآیند الکترولیتی، یک لایه پیوسته از آلومینیوم را روی سطح کاتد نشان داد که نشان‌دهنده ترشوندگی قابل قبول است. وجود TiC/TiB_2 با آنالیز فازی اشعه ایکس و آنالیز ساختاری اشعه ایکس آنالیز (SEM-EDS)تأیید شد. فناوری‌های نوآورانه ارائه شده برای تولید مواد الکترود کامپوزیتی می‌توانند برای سنتز طیف وسیعی از محصولات کامپوزیتی در سیستم $C - MeC/MeB2$ مورد استفاده قرار گیرند. مقدار معادل کک نفتی و اکسیدهای فلزات نسوز، امکان فرض دوره بازگشت سرمایه کوتاه استفاده از بلوک‌های کاتد کامپوزیتی در گلدان‌های موجود و در گلدان‌های در حال طراحی را فراهم می‌کند.