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Problems and solutions to protection of carbon-graphite electrodes

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Abstract. This paper presents literature review of the existing problems and solutions in protecting carbon-graphite electrodes from the destructive environment of arc steel-making furnaces, magnesium and aluminum cells. The most significant publications on the corrosion resistance of cathodes and anodes in relation to physical, chemical, and electrochemical wear, to oxidizing environments, to active components of the introduction and destruction of the carbon structure are discussed. An analysis of various proposals and engineering solutions for reducing or eliminating the impact of aggressive environments on electrodes under specific operating conditions of metallurgical units is carried out. It was established that losses from lateral oxidation of the electrode surface of arc steel-making furnaces, when passing the temperature zone of 600–800 °C, may reach 40–60% of the total consumption. Carbon-graphite products are subject to a significant destructive effect of the specific interaction of carbon with elements and compounds of the working environment, which can be introduced (intercalate) into the interlayer structure of carbon. The existing engineering and technological solutions mainly apply to the protection of the product surface; moreover, they perform their functions for a short time, rather than during the entire service life of the metallurgical unit. In this connection, it is proposed to focus on ensuring volumetric protection of electrodes from the effects of an aggressive environment. Intermediate results obtained in the field of synthesis of carbon-based composite materials adapted to the conditions of electrode production at existing enterprises are presented, along with the results of studies into the oxidizability of these composites. The existing and proposed engineering solutions for protecting the surface of carbon products have not received wide recognition or are not used in the metallurgical industry. Among the most probable reasons are the limited period of electrode surface protection, the complexity of reproduction, or the lack of profitability due to the high cost of protective components. In this regard, synthesis of C – TiC/TiB2 composite electrodes based on petroleum coke and graphite seems to be a promising research direction.

Keywords: carbon-graphite electrode, material destruction, oxidation, wear, intercalation, protective coatings, composite materials

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МЕТАЛЛУРГИЯ

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Проблемы и решения защиты углеграфитовых электродов

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Резюме. Цель – литературный обзор существующих проблем и решений по защите углеграфитовых электродов от деструктивного воздействия агрессивной среды дуговых сталеплавильных печей, магниевых и алюминиевых электролизеров. В работе приведено обсуждение наиболее значимых результатов исследований коррозионной стойкости катодов и анодов по отношению к физическому, химическому и электрохимическому износу, окислительной среде, а также к активным компонентам внедрения и разрушения углеродной структуры. Проведен анализ предложений и технических решений по уменьшению или исключению воздействия агрессивной среды на электроды в конкретных условиях работы металлургических агрегатов. Установлено, что потери от бокового окисления поверхности электродов дуговых сталеплавильных печей при прохождении температурной зоны 600–800°С достигают 40–60% от общего расхода. Значительное разрушающее воздействие

на углеграфитовые изделия оказывает специфическое взаимодействие углерода с элементами и соединениями рабочей среды, способными внедряться (интеркалировать) в межслойную структуру углерода. Существующие технические и технологические решения распространяются на защиту поверхности изделий и выполняют свои функции в течение короткого времени, но не в течение срока службы металлургического агрегата. Предложено сконцентрироваться на обеспечении объемной защиты электродов от воздействия агрессивной среды. Представлены промежуточные результаты перспективного направления синтеза композитных материалов на основе углерода, адаптированного к условиям производства электродов на действующих предприятиях, а также результаты исследования окисляемости этих композитов. Существующие и предлагаемые технические решения по защите поверхности углеродных изделий не получили широкого признания, либо не используются в металлургической отрасли. Вероятная причина – ограниченный период защиты поверхности электродов, сложность воспроизведения или отсутствие рентабельности из-за высокой стоимости защитных компонентов. В этой связи для обсуждения предложено перспективное направление создания коррозионно-стойких материалов – синтез композитных электродов C – TiC/TiB_2 на основе нефтяного кокса и графита в стандартных условиях промышленного производства.

Ключевые слова: углеграфитовый электрод, деструкция материала, окисление, износ, интеркаляция, защитные покрытия, композитные материалы

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INTRODUCTION

One of the most recent problems in up-to-date technologies of structural materials production is an increase of their stability in aggressive environment, a prolongation of service life of heavy-duty pieces and metallurgical units in the whole. To the full extent this relates to carbon-graphite materials that are widely used in the production of ferrous and non-ferrous metals. They have to retain in a continuous and reliable manner their functional properties in conditions of high temperatures and pressures, oxidizing environment, high dynamic and static loads. In this regard, the initial materials [1, 2], combinations of fractional size distributions [3, 4], binding components and modifying additives are subject to special requirements in terms of composition [5–7], emissions of gaseous and solid components [8–10].

The offered overview discusses most important results of multiple investigations concerning the conditions of carbon and graphite products use in electric arc steel-making furnaces, magnesium and aluminium cells. In this respect the overview shall emphasize special methods and measures for the protection of carbon-graphite materials against gas and electrochemical corrosions, erosion wear and degradation at the formation of inter-layer (lamellar) compounds. In this regard we shall preliminary note some particular features of graphite structure and its interaction with aggressive environment.

GRAPHITE STRUCTURE

Theoretical density of graphite is 2265 kg/m^3 [11, 12]. Under ordinary conditions it is resistant to the action of acids and salt solutions; it does not interact with nitrogen, chlorine and other elements. The graphite structure is one of the first to be studied using methods of X-ray crystal structure analysis [13–15]; moreover, with the development of experimental technologies, the accuracy of such measurements increased [16–18]. According to these data the carbon atoms are located in graphite in parallel layers, the distance between which under room temperature is d0 = 3.3538 Å (Fig. 1). In each flat layer carbon atoms form the lattice of regular hexagons with C-C distance of a0=1.415 Å. Carbon atoms within the layer are bound by strong covalent bonds having a binding energy of 167.6 kJ/mole. The interaction between layers is carried out by weak Van der Waals forces having a binding energy of 16.75 kJ/mole at the temperature of 15°C [12]. Thus, individual layers can separate easily from the crystal, which is widely used while fabricating any antifriction and sealing products but substantiates their considerable physical wear.

Three main types of graphite have a nearly ideal structure: natural graphite, Kish-graphite and highly oriented pyrolytic graphite (HOPG) [20, 21]. Real structures of graphites and materials having a graphite-like structures differ from ideal ones by presence of different defects. Artificial graphites with less ordered structures are usually produced

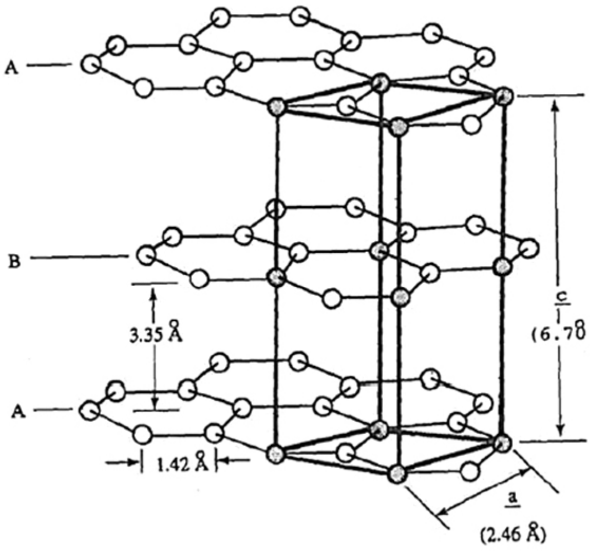

Fig. 1. *Crystal structure of hexagonal graphite [19]*
Рис. 1. *Кристаллическая структура гексагонального графита [19]*

from petroleum coke and coal tar pitch[6] [22, 23]. Billets are molded by method of extrusion or pressing. Produced billets are exposed to the step-wise thermal treatment without air access (up to 1300–1500°C) and then to the graphitization (up to 2400–2700°C).

AGGRESSIVE ENVIRONMENT IMPACT

Along with unique operation properties of carbon-graphite products (acceptable strength, high heat resistance, electrical and heat conductivities) there are some particular features that require the protection of this material against any aggressive environment impact.

Oxidation. Air oxidation of carbon graphites starts already at 400–500°C, and under temperatures exceeding 1200°C it takes a catastrophic form, including their complete burn-out [24, 25]. Kinetic parameters of oxidation are well known [26, 27]. It is considered that under low temperatures the limiting stage is a chemical reaction, under high temperatures this is an external diffusion, and in the interval between them – internal diffusion. It is supposed that the reactive capability of carbon material to the large extent depends on the perfection of crystalline structure being characterized by inter-planar distance and by size of crystallites [28, 29]. With the growth of the first parameter the reactive capability falls, and the growth of the second parameter causes its increase. In addition, the oxidizability of graphite is significantly influenced by presence of impurities, which could serve as catalysts for the process. The impurities of some metals, like iron, copper, vanadium, sodium have an especially strong influence.

Intercalation of graphite. Practically all carbon and graphite products in different operation conditions are exposed to the degradation at the specific interaction with alkaline and alkali-earth metals, their fluorides, chlorides and bromides, with acids and halogens. It concerns the penetration (intercalation) of the atoms or molecules of above mentioned components between structural planes of graphite. Material that was formed at this area is called «graphite intercalation compounds GIC» [30, 31]. This specific phenomenon is interesting for us in that during the interaction of carbon-graphite materials with components, penetrated into the host crystalline lattice, the expansion and swelling of carbon product takes place, which has sometimes catastrophic destructive consequences.

Relatively weak forces acting between graphite layers predetermine the possible penetration of different substance matters into the graphite matrix and the formation of interlayer carbon compounds. Currently, GIC with various substance matters have been well studied, which, according to the type of interaction of penetrated components (intercalants) with the graphite crystalline lattice, can be split into two main groups [32] (Fig. 2):

1. Acceptor GIC, in which polyarene lattices bear a positive charge and represent macro-cations C_n^+. This group includes compounds with (sulphuric, nitric and other) acids [33], with fluorides, chlorides and bromides of metals[7] and with halogens [34]. It also includes covalent laminar compounds

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[6] Marmer E.N. Carbon-graphite materials: reference manual. Moscow: Metallurgy, 1973. 135 p. / Мармер Э.Н. Углеграфитовые материалы: справочник. М.: Металлургия, 1973. 135 с.

[7] Novikov Yu.N. Synthesis and study of layered compounds of graphite with transition metals and their salts: author's abstract of Cand. Sci. (Chem.) Dissertation. Moscow, 1971. 19 p. /Новиков Ю.Н. Синтез и исследование слоистых соединений графита с переходными металлами и их солями: автореф. дис. ... канд. хим. наук. М., 1971. 19 с.

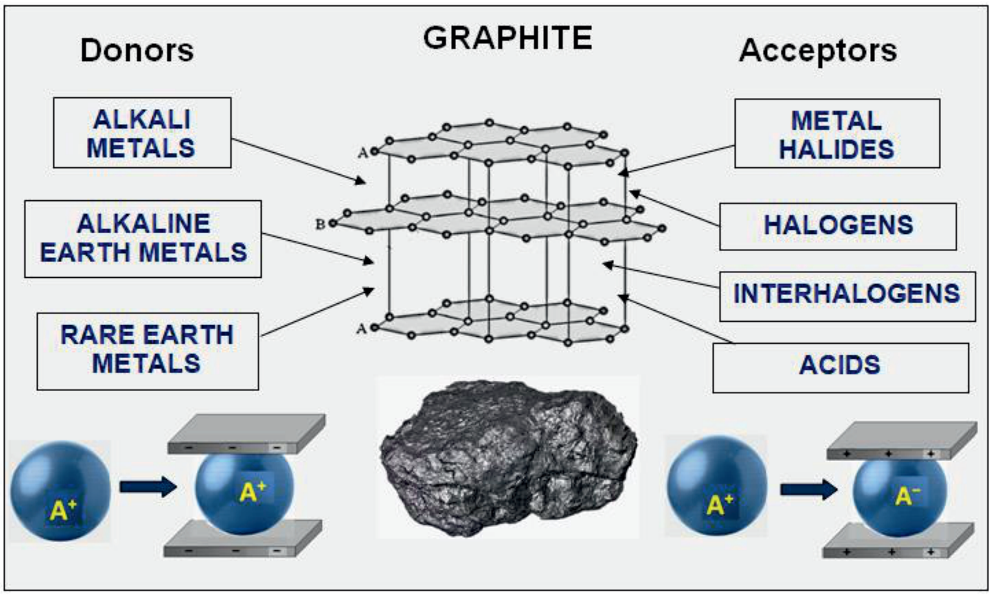

Fig. 2. *Graphite intercalation reactions*[8]
Рис. 2. *Реакции интеркалирования графита*[8]

with oxygen and fluorine, in which as opposed to all other GIC the bonds of intercalant with polyarene fragments are covalent [35].

2. *Donor GIC,* where the intercalant acts as donor of electrons, and graphite layers are macro-anions C_n^-. This group includes GIC with alkaline and alkali-earth metals [36].

The GIC composition is usually given by formulas of C_nM type, where n – number of carbon atoms per molecule M of intercalant. The GIC structure is characterized by number of carbon layers that are between the layers of penetrated intercalant [33, 37].

Besides the gas corrosion and destruction under the GIS influence, the carbon-graphite electrodes in electrolytic processes are exposed to physical, chemical and electro-chemical wear, which rate is also determined by perfection degree of carbon crystalline structure. It will be more convenient for us to discuss this type of corrosion wear when considering specific conditions of electrode application.

ELECTRODES FOR ELECTRIC ARC STEEL-MAKING FURNACES

Steel-making processes mostly use graphitized electrodes that possess higher physical-chemical and electrical properties than carbon electrodes. To produce such electrodes, needle petroleum coke is mostly used as well as returns of this production process. Coal tar pitch for electrodes is used as binding agent. Graphitized electrodes are characterized by low specific electrical resistance of 8–13 μΩ m and by porosity of about 20%, by high thermal resistance and strength of 20–40 MPa; they contain little ash. The admissible current density in these electrodes makes 28, 16 and 14 A/cm^2 with diameters of 150, 400 and 550 mm respectively. In special graphitized electrodes it achieves 50 A/cm^2.

Main criteria for the evaluation of electrode operation is its specific consumption. With a gradual progressive movement in the temperature zone of 600–800°C the side surface of electrodes is exposed to oxidative attack of gas environment. Losses from side oxidation make 40–60% from total amount of losses [38–40]. Thus, the diameter of electrode reduces, i.e. in working zone the current density increases.

Ways to reduce the consumption of electrodes. In the cost price of the output the share of electrodes makes 8–12% [40], which stimulates the investigations on their

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[8] Ionov S.G. Electron transport and physicochemical properties of intercalated compounds of graphite and carbon materials based on them. Moscow, 2016. /Ионов С.Г. Электронный транспорт и физико-химические свойства интеркалированных соединений графита и углеродных материалов на их основе: автореф. дис. … д-ра ф.-м. наук: 01.04.2016. М., 2016.

consumption reduction. One of this work directions consists in applying the corrosion and erosion resistant coating on the side surface of electrode for its protection against the oxidation. If use coated electrodes with diameter of 610mm in electric arc furnaces with capacity of 140–180 tons and current intensity of 35–68 kA, savings shall make 16–23%, for electrodes with diameter of 508mm savings shall make 27% (in comparison with non-coated electrodes) [41]. In the work of reference, the specimens of laboratory graphite were investigated with protective coating and without it. Initial graphitized specimens were produced based on needle and ordinary petroleum cokes, which oxidizability made 51.4% and 54.6% respectively. When coatings based on Al_2O_3, SiO_2, SiC and silicomanganese (MnC-17) in form of 50% liquid glass suspension were applied, the oxidizability reduced at 850ºC on 18.7 (Al_2O_3) – 63.8% (SiC) in comparison with specimens without coating.

Similar coatings were used for graphite in works of other researchers. In many patents protective coatings are proposed to be formed from refractory oxides and carbides of aluminium, boron, titanium, zirconium [42, 43], tantalum, chromium and silicon [44–46] using slip painting or pulverization, after preliminary vacuum degassing or under pressure with subsequent drying and reactive sintering [47, 48]. In all cases the efficiency of the methods was registered during the operation of electrodes.

In order to optimize protective compositions known coating methods were analyzed. Paper [49] noted that aluminium-based coatings reduce the specific consumption of electrodes on 10–12%, and those based on ferrosilicon of FS45 grade – on 20% in comparison with electrodes without coating. The research paper [50] proposes two-layer coating, which first layer consists of aluminium or its alloy, the second one – of copper. Coated electrode is treated with electric arc or plasma burner. According to the electrode protection method [51], tested in semi-industrial conditions in order to reduce the oxidizability, the composite coating, based on silicon and tungsten shall be applied onto graphite by electrical precipitation; in order to reduce the electric resistance the protective coating based on electrolytic copper shall be applied. To protect graphite electrodes against oxidation LLC «BBCT» proposes two-layer coating based on iron aluminide with total thickness of 0.1–2.0 mm [52, 53]. The first layer is applied by method of arc metal coating, using solid wire made of aluminium or its alloy, containing 5–10% of silicon. The second layer is done using flux-cored wire consisted of steel shell and core made of the charge, containing (% wt.): aluminium (15.0–20.0), chromium (2.0–6.0), yttrium (0.5–3.0), iron – matrix. Inventions allow to increase the resistance of graphitized electrodes operating in conditions of high-temperature corrosion, and to reduce their oxidation and consumption.

In papers [54, 55] the ZrB_2–SiC–$TaSi_2$–Si coating was synthesized on the support of siliconized graphite using the combined process of applying the suspension with the brush and infiltration of silicon vapors. It was found out that oxidation kinetics at 1500 °C in static air atmosphere complies with parabolic law having a relatively low constant of oxidation rate down to 0.27 mg/(cm$^{2}\cdot$h^{0,5}). Determining factor was a high strength of transition SiC layer adhesion to the graphite support and external ZrB_2–SiC–$TaSi_2$–Si layer.

According to other common method for the protection of carbon and graphite electrodes against oxidation, electrodes are treated with water solution of sodium polyphosphate with concentration of 18–20% wt. and maleinic acid with concentration of 0.05–0.1% wt. at the temperature of 90–100 °C[9]. According to the description [56] the method supposes to increase the oxidation resistance of graphitized electrodes by treating the surface of electrodes with penetrating salt solution, based on phosphoric acid: water – 20–25% wt.; H_3PO_4 – 30–35% wt.; $MnHPO_4 \cdot 1.6\, H_2O$ – 0–15% wt.; $Al(H_2PO_4)_3$ – 2–15% wt.; B_2O_3 – 0.5–2.0% wt.; $Zn_3(PO)_2$ – 1–7% wt.

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[9] Kuzmenkov M.I., Shishko N.Ya., Surovtseva I.B., Kabanenko S.N. A method to protect carbon and graphite electrodes from oxidation. A. s. USSR, no. 1699909; 1991. Bulletin no. 47. /А. с. № 1699909, СССР, С01 В 31/02. Способ защиты угольных и графитовых электродов от окисления / М.И. Кузьменков, Н.Я. Шишко, И.Б. Суровцева, С.Н. Кабаненко; Белорусский технологический институт им. С.М. Кирова. № 4766489/26. Заявл. 09.11.1989; опубл. 23.12.91. Бюл. № 47.

and mono-, di- or triple-base phosphate of alkaline metal (10–20%wt.) According to joint patent of Belorussian metallurgical plant and Novocherkassk electrode plant the optimal results were obtained when applying protective coating by spraying water solution of nitride-boron-phosphate composition (ammonium salt of phosphoric acid and boron acid: $(NH_4)_2HPO_4$ – 5–15% wt., H_3BO_3 – 3–10% wt., water – the rest) on graphite [57]. The destructibility of treated specimens in CO_2 atmosphere at 1000°C for one hour made 11–13%, while check test pieces shown mass losses of 25–27%. In patent of JSC «Energoprom-NEZ» dated 2013 [58] the impregnation of heated graphitized products with solution that protects against the oxidation, is done gradually with preliminary vacuum degassing and subsequent supply of solution under pressure of compressed gas.

ELECTRODES OF MAGNESIUM CELLS

Main process units in the production of crude magnesium are diaphragm-less electrolytic cells with top and bottom input of graphite anodes [59]. Graphite materials suffer destructive changes in electrolytic bath and in gas phase of chlorine-containing media within various temperature zones, which limits the service life of the whole unit. The time between repairs of electrolytic cells with top and bottom input of graphite anodes makes 39–40 and 45–48 months respectively.

Protection of magnesium cell anodes against the oxidation

Work has been undertaken and is continuing to reduce the effects of the gas oxidizing environment on graphite anodes. During the period of 1969–1980 these efforts purposed the limitation of air access to anodes and the improvement of working zone ecology. Magnesium cells with top input of anodes were proposed to be protected by pouring the anode block with heat-resistant low-porous concrete around the entire perimeter[10]; by sealing the contact of concrete floor with anodes with corundum-containing material [60] or its mixture with structure-sealing powder material at the ratio of 3:1[11]. During the period of cell start-up and achievement of the temperature of 480°C this material melts and seals hermetically the space between the anode and the floor.

The other direction in the protection of anodes against the oxidation consists in the impregnation of their surface with protective inhibitor solutions. Solutions, based on phosphoric acid with boron containing additives are most often used [56–58]. In papers [61–69] the possibility to use water solution of the mixture of zinc ($Zn(H_2PO_4)_2{\cdot}2H_2O$) and aluminium ($Al(H_2PO_4)_3{\cdot}2H_2O$) dihydrophosphates in orthophosphoric acid was studied. The oxidation resistance of impregnated and non-impregnated graphiite specimens was evaluated in laboratory conditions according to the resultsof holding process at the temperature of 700°C in dynamic air current for 200 min. It was defined that the oxidation rate of non-impregnated and impregnated graphite specimens made 27.2 and 5.52 $g/cm^2{\cdot}h$.

Oxidation and wear within the electrolytic bath. Along with the oxidation of anodes over the electrolytic bath surface their oxidation and wear takes place within the bath volume by virtue of oxygen precipitation on the anode. Patent of Novocherkassk electrode plant dated 1973 presents[12] the method for treatment of graphite anodes with oxyethylated amide of

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[10] Burdakov Yu.M., Kolomiytsev A.V., Tretyak S.D., Chalabaev I.A. Method to protect anodes of a magnesium electrolyzer with top anode input. A. s. USSR, no. 259397; 1969. /А. с. № 259397, СССР, С 25С 3/04. Способ защиты анодов магниевого электролизера с верхним вводом анодов / Ю.М. Бурдаков, А.В. Коломийцев, С.Д. Третьяк, И.А. Чалабаев; № 1233784/22-1. Заявл. 15.04.1968; опубл. 12.12.1969.

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[12] Fokin V.P., Kralin L.A., Zarechenskij E.T., Hentov V.Ya., Semin E.G., Petrova N.I. Graphite anode processing method. A. s. USSR, no. 384542; 1973. Bulletin no. 25. /А. с. № 384542 СССР. В01к 3/08. Способ обработки графитовых анодов / В.П. Фокин, Л.А. Кралин, Е.Т. Зареченский, В.Я. Хентов, Е.Г. Семин, Н.И. Петрова; Новочеркасский электродный завод. № 1496168/23-26. Заявл. 01.12.1970; опубл. 29.05.1973. Бюл. № 25.

synthetic fatty acid followed by impregnation with emulsion of lenseed oil. The total wear of anodes reduces from 74.3 to 62 mg/a·h.

In the description of the method, developed by author's collective from JSC "AVISMA titanium-magnesium complex" in 1999, it is proposed to treat electrodes in two stages successively: first, the impregnation in the melt of metaphosphates with subsequent drying in drying chamber at 300°C, and then the treatment in the electrolytic bath of magnesium cells at the current density of 0.20–0.45 A/cm^2 and melt temperature of 670–700°C, applying the anode potential [63]. After such treatment the rate of oxidation-wear of the bottom anodes reduces from 1.5 to 1.14–1.20 mm per month, their serviceability being increased from 24 to 37 months respectively.

The interesting method for the reduction of bipolar graphite anode wear rate is presented in patent [64]. Authors propose to protect bipolar electrodes of magnesium cell by using cataphoretic precipitation of magnesium oxide film onto the cathode surface in the electrolytic bath with temperature of 500–630°C and magnesium oxide and magnesium chloride content of 0.21–5% wt. and 25.1–70% wt. respectively.

Authors [65] confirm the problem of anode wear in the electrolytic bath, which causes the increase in voltage, energy consumption and process temperature, resulting in metal losses, i.e. decline in production and finally shutdown of the cell. Due to this, the wear of graphite anodes was studied by method of confocal profilometry of the surface in laboratory magnesium cell with vertical electrodes. Specimens of 4 types of graphite anodes were exposed to the electrolytic process for 24 hours at the temperature of 690–710°C and current density of 1 A/cm^2 in the melts having high content of oxides (MgO and $MgOHCl$). The influence of following parameters: oxide concentration, type of oxide and type of graphite on the anode wear was studied. It was supposed that the wear of anodes in electrolytic bath, based on $MgCl_2$ occurs according to the following mechanism:

$$xMgO + C = CO_x + xMg^{2+} + 2\bar{e} \qquad (1)$$

In addition, it was admitted that at the same time the physical erosion of anode surface takes place due to the circulation of electrolyte, which composition comprises suspended particles of oxides. At the initial level of oxides in the melt, making 1400 and 9000 ppm, the wear losses for 24 hours made 17 and 47 mcm respectively. The study of the influence of oxide type shown that the wear of graphite anodes is two times lower when the melt contains MgO than when it contains $MgOHCl$ (Table 1).

From data obtained it follows that the grain size of graphite, the density and strength of products have a decisive influence on the wear resistance of anodes in chloride melts.

Intercalation of the anodes of magnesium cells. Results of the study on the behavior of carbon anodes in the melts of chlorides, containing 61 mol. % $AlCl_3$ and 39 mol. % $NaCl$, show that carbon anodes decompose easily at 200°C by intercalation compounds that are formed at the considerable volume expansion of carbon material [66]. The temperature increase, exceeding 600°C makes GIC less stable and, consequently, slows down the decay of material. In chloride melts without $AlCl_3$ the rate of electrode wear with chlorine emission is significantly lower. In these technical conditions anodes rather destroy under the oxygen effect than as a result of anode chlorine corrosion. This may serve as an explanation of observed carbon anode stability in magnesium cells.

Paper [67] studied the erosion-corrosion decomposition of some technical carbons, including glass carbons, under chlorine effect

Graphite anode wear after 24-hour electrolysis [65]
Износ графитовых анодов за 24 ч электролиза [65]

Grade of SGL graphite	Grain size, μm	Apparent density, g/cm³	Flexural strength, MPa	Open porosity, %	Ash content, ppm	Wear μm
R8710	3	1.9	85	10	200	7
EK20	30	1.7	55	11	75	10
R4180	40	1.7	25	16	2000	30
SGL standard	220	1.69	29	25	290	24

at the temperature range from 600 to 800 °C. It is found out that chloride corrosion is a very slow process: the loss of carbon mass in chlorine atmosphere has a rate of about 0,5 mm/year at the temperature of 800 °C. It is noted that the combustion in oxygen atmosphere takes place by five orders of magnitude faster than the chloride impact on carbon.

Article [68] describes the study of anode chlorine corrosion of the technical carbon under two different conditions:

I. Medium-temperature (from 200 to 300 °C) carbon corrosion of anode in mixed chloride-alkali melts (LiCl/NaCl, LiCl/KCl), to which aluminium chloride is added at the ratio of $AlCl1_3/MeCl > 1$. Authors came to the conclusion that in these conditions intercalation compounds $C_{10}(AlCCl_3)_xCl_{0.136}$ are formed at the anode polarization of graphite specimens. The destruction of graphite anode occurs, the degree of carbon conversion into intercalation carbon is close to 40%.

2. High-temperature (from 600 to 800 °C) chloride corrosion of anode in main smelts of alkali metal chlorides ($MeCl_2$) with addition of 10 mol. % aluminium chloride and without it. Main task is to study high-temperature stability of chlorine-emitting anodes. It was found out that with increase of temperature within the range of 600–800 °C Acheson graphites become more stable; considerable wear was not observed in chloride melts, including in the presence of $AlCl_3$. However, at the current densities exceeding 0,2 A/cm^2 the consumption rate of carbon anodes increases in the presence of tetra-chloro-aluminate anions, i.e. in main mixed melts of alkaline chlorides and aluminium chloride. At the technical current density of 0,4 A/cm^2 and at the temperature of 700 °C the corrosion rate is estimated to be equal to several centimeters per year, which makes carbon anodes unstable in size.

Paper [69] used methods of cyclic voltammetry (CV) and electronic microscopy, for the investigation of the impact of NaCl-KCl-$MgCl_2$ electrolyte at 700 °C and that of chlorine intercalation on anode specimens made of three different types of graphite – needle coke (NC), fine petroleum coke (FPC) and common petroleum coke (CPC) respectively. It was found out that the specimens of graphite anodes from NC have the best resistance to chlorine intercalation and to electrolyte impact. Specimens of common CPC were subject to the highest chlorine intercalation and electrolyte impact. To the authors mind, this is related to the presence of impurities in that coke, which could act as catalysts of chlorine intercalation and electrolytic corrosion.

In other words, the presence of impurities in graphite anode (for example, Fe, Al and others), or the penetration of these impurities into the anode during the operation can initiate their chlorination to metal chlorides ($FeCl_3$, $AlCl_3$) with subsequent destructive processes for anode in low-temperature zone.

ELECTRODES OF ALUMINIUM CELLS

Wear of cathode blocks (bottom). The main cause of premature failure of up-to-date cells is wear of graphite cathodes [70–72]. Observations over electrochemical and physical wear of the bottom can be systematized as follows:

- The wear rate increases with increase of current density and smelt circulation speed, with decrease of metal level and cryolite ratio;
- Local wear increases with increase of block graphitization level.

According to data of [73, 74] the wear rate of cathode blocks in industrial cells makes:

– 0.5–1.5 cm/year – for anthracite blocks,
– 1.5–2.5 cm/year – for graphite and graphitized blocks.

According to results of other investigations, presented in patent [75], following wear rates for different materials were registered:

– 1.0–2.0 cm/year – for semi-graphitized material,
– 2.0–4.0 cm/year – for graphitized material,
– 4.0–8.0 cm/year – for graphite material.

This means that the intensification of electrolytic reduction process, the increase of cell capacity and the change-over to graphite cathode blocks require new approaches to material composition of electrodes.

Intercalation of aluminium cell cathodes. The fundamental work of Michael B. Rapoport underlines that after sodium penetration the distance between layers increases from 3.35 Å to 4.6 Å, after potassium penetration it increases to 5.4 Å, after that of cesium – to 5.95 Å [76]. This phenomenon is behind the swelling of carbon substance and in some cases its complete destruction. It is deemed that in descending order of resistance to sodium influence carbon materials are arranged in following sequence: graphite, anthracite, foundry coke, pitch coke, petroleum coke.

The penetration process takes place within a certain range of temperatures, that likely depends on reagent vapor pressure. It is generally accepted that the following reaction is the main source of sodium [77]:

$$\mathrm{Al} + 3\mathrm{NaF}_{\text{(in electrolyte)}} = \mathrm{AlF}_{3\text{(in electrolyte)}} + 3\mathrm{Na}_{\text{(in carbon)}} \quad (2)$$

$$\mathrm{Na}^{+}_{\text{(in electrolyte)}} + 1\bar{e} = \mathrm{Na}_{\text{(in carbon)}} \quad (3)$$

From these equations and polarization conditions it is evident that the activity of sodium and its transfer within the volume of carbon products is intensified with increase of cryolite ratio, current density and temperature; being accumulated on the borders of temperature isotherms. Under appropriate temperature and concentration conditions the interaction occurs between carbon and intercalate to form compounds between them ($C_n^- K^+ \cdot 2K$, $C_n^- Na^+ \cdot 2Na$,) with subsequent volume expansion of carbon material and potentially complete or local destruction of electrodes. When conditions change (slight increase of the temperature, changes in gas environment, humidity and others) the reaction reversibility can occur, producing carbon substance in form of graphite. This process is called low-temperature or "abnormal" graphitization of amorphous carbon. It is found out that at the cryolite ratio of 2.3–2.7 and industrial current densities the expansion of blocks from amorphous carbon makes 4.0–4.5% [78].

Investigations of M.B. Rapoport, carried out in 50-60-s intensified investigations related to the electrolytic reduction of molten salts and to the interaction of electrolyte components with carbon-graphite materials. These investigations were evidenced in extensive reviews and books of foreign and Russian scientists [59, 79, 80]. All of them come to that in practice various types of carbons have completely different structures possessing different susceptibility to the interlayer penetration of sodium [81, 82]. Deviations in moving force to interactions between intercalate and carbon are explained by changes in Fermi characteristic energy level that has an influence on π – carbon bonds. The low Fermi characteristic energy level was observed for low-ordered carbons, which is favorable for the transfer of electrons, for example, from sodium to carbon. Graphites with high Fermi characteristic energy level show the tendency towards the bonding with acceptors of electrons, and therefore they are less reactively active with regard to alkaline metals. However, they are susceptible to the penetration of aluminium chlorides $AlCl_3$ and iron chlorides $FeCl_3$, for example.

It is evident that any method, used for the reduction of intercalate penetration rate and also for the increase of electrode material strength, shall be of importance to increase the service life of metallurgical units.

Protection of aluminium cell electrodes against oxidation and wear

Protection of carbon anodes. Carbon anode of aluminium cell is formed from anode paste, consisted of petroleum coke and binding material (coal tar pitch).

The protection of carbon anode surface is mostly associated with additives and impregnating solutions, based on boron-containing compounds. Paper dated 1968 [83] defined optimum concentrations of boron oxide in anode based on changes in oxidizability and friability characteristics, anode consumption and back electro-motive force during the electrolytic reduction process. While studying oxidizability and friability characteristics under CO_2 at the temperature of 950 °C it was found out that the most profitable B_2O_3 concentration is 1% (per mass of binding agent), as it is possible to expect a decrease in oxidizability by about 2 times two-times (from 0.22 to 0.1 g/cm^2·h) and in friability by more than 10 times (from 0.19 to 0.01 g/cm^2·h). It is noted that the inevitable consequence of reactive anode capability decrease is the increase of anodic overvoltage, which takes the form of back electro-motive force increase from 1.6 V for anode without additives to 1.7 V for anode with 1% wt. B_2O_3 additive.

In 1972 the batch of anode paste with additive of 0.6% H_3BO_3 (1% to pitch) was produced at Novocherkassk electrode plant [84]. The pilot paste in amount of 300 tons was tested in three Soderberg cells of VgAZ (Volgograd Aluminium Smelter) during the period of five months. The application of pilot paste did not affect any parameters of anodes, but resulted in their consumption reduction on approx. 8% (40 kg/t), and the rate of pilot anode combustion reduced on 6% in comparison with ordinary paste. Measurements of voltage drop in anodes demonstrate that ΔU_a of anodes from pilot cells is on approx. 40 mV lower than on the cells with standard anodes.

In patents of 2000 and 2010 [85, 86] boron oxide B_2O_3 and orthoboric acid H_3BO_3 were also chosen as basic material for the protective coating of anode surface. The mixture of boron-containing compounds was applied onto the surface in form of slurry – concentrated suspension or paste that solidified at the temperatures exceeding 300 °C. The protective properties were tested under CO_2 and good protective properties of the composition were discovered in the CO_2 + AlF_3 mixture.

Paper [87] gives results of studies on the impregnation of specimens of finished prebake anodes, promising for aluminium cells, with organic compounds. 5, 10 and 20% solutions of bitumen in hexane and compositions of «Silor-Ultra» grade were used as organic liquids. The process of anode impregnation was carried out after preliminary vacuum degassing of the reservoir. It follows from the results of the corrosion resistance tests of laboratory specimens in cryolite-alumina melts under electrolytic that the most stable specimens were specimens with specific consumption of 0.217–0.278 g/(A·h), impregnated with «Silor-Ultra» composition. Specimens, impregnated with 5% solutions of bitumen in hexane demonstrated the highest consumption of anode material.

Patent of 2010 [88] presents an original method of the impregnation of carbon-graphite anode with molten electrolyte. To do this, during the electrolytic reduction process, the polarity of the anode is changed for 10–15 min during the day, then the anode and cathode are polarized with working current under normal conditions. Preliminary experiments in the laboratory environment shown that the impregnation with melts achieves the depth of 30–40 mm over the period of 10 min. Such depth of impregnation is less than the burnout thickness of carbon anode bottom part (20–25 mm) per day of cell work. This method provides the increase of the cell service life and the improvement of technological process.

Protection of carbon cathodes. As it was discussed earlier, the graphite block is proof against the action of alkali metals, but these stable forms of carbon are expensive and subjected to significant wear. From the other side less expensive amorphous blocks are excessively subjected to the attack of sodium but not lithium. Therefore, researchers had an idea of preliminary carbon material saturation with lithium or its compounds. To increase the resistance of the cell to the aggressive environment impact they propose the treatment of cathode carbon products at the temperature of 950 °C with lithium vapors [89], with lithium fluoride [90] or other lithium-containing compounds (for example, with water solution of lithium acetate) [91]. In all cases the mitigation of sodium impact on cathode materials was observed during their subsequent tests in sodium-containing melts.

Due to high level of wear the authors of patent dated 2005 [75] proposed the impregnated graphite cathode for aluminium reduction process and the method of its fabrication. The method comprises the block graphitization at the temperatures exceeding 2400 °C, its impregnation by immersing in a vacuum into coal tar or petroleum pitches and subsequent thermal treatment at the temperature less than 1600 °C. Measurements of apparent density and flexural strength shown their increase on 9.5% and 63.5% respectively in comparison with non-impregnated blocks. Technical result was an increase of service life of graphite cathode.

Another popular direction in carbon cathode protection is an application of refractory metal compounds, wetted with aluminium (for example, with titanium carbide or diboride – TiC or TiB_2). In some cases these refractory metal compounds are applied by any method onto the cathode surface before the cell startup [92–94], in other cases they are electrically precipitated during the electrolytic reduction process [95]. The detailed study and discussion of these directions, carried out from 1930-s to 2022, are given in monography [96] and review [97].

In most cases researchers confirm the effectiveness of cathode protection with refractory compounds in laboratory conditions or at pilot tests on industrial sites. However, no one of world corporative scientific research centers solved these problems completely and finally. Available alternatives were not accorded wide recognition or they are not used in metallurgical branch. The answer on the question «Why?» is clear: these proposed solutions are efficient in laboratory or short pilot tests. These solutions cover the surface of the products and fulfil their functions during a short period of time but not during the whole service life of a metallurgical unit. Surface and near-surface protective impregnation is taken away with gases and it crumbles; and coatings peel off as a result of cyclic thermal expansion and shrinkage processes. In addition, the scaling in industrial conditions of production and operation demonstrates the complexity of their implementation or lack of profitability due to the high cost of protective components.

In other words, as it is clear from previous review, carbon products as electrodes for metallurgical units require extensive and long-term protection. Due to this and based on the analyses of the results of previous investigations and practical works the synthesis of composite carbon-based materials shall be considered as promising direction for the creation of electrodes, corrosion-resistant in aggressive environment. The solution of these tasks, separately or in the whole, shall allow starting the design and construction of metallurgical units of new generation.

COMPOSITE ELECTRODES

In scientific center of «Problems of mineral and anthropogenic resources processing», Saint-Petersburg Mining University, the possibility in principle to synthetize composite materials of carbon – carbide /titanium diboride (C – TiC/TiB_2), based on petroleum coke and graphite, was explored. The synthesis technology was adapted to existing conditions of carbon-graphite goods production at electrode plants. Following initial titanium- and boron-containing components were used for the development of the electrodes:

- Based on petroleum coke – titanium metal Ti and boron oxide B_2O_3.
- Based on natural graphite – solutions of titanium sulphate $Ti_2(SO_4)_3$ and boron acid H_3BO_3.

Synthesized components were studied in terms of their behavior in oxidizing environment.

Composite electrodes, based on petroleum coke. To develop $C_{petroleum.coke}$ – TiC/TiB_2 electrodes in laboratory conditions, the standard procedure of mixing initial materials, their pressing and baking was used. Calcined petroleum coke with particle size of not more than 2 mm, titanium metal powder, boron oxide and coal tar pitch (13–15% wt.) were mixed in the mixer at the temperature of 135±5°C for 15–20 min. After molding on the static press at the pressure of 15–20 MPa “green” specimens were subjected to the baking in muffle furnace at the temperature of 1050±10ºC under the layer of petroleum coke within the space of 3 hours. In such way the conditions for baking carbon-graphite products in industrial furnaces were to some extent simulated; and the partial oxidation of synthesized TiC/TiB_2 compounds within the carbon body was admitted.

Fig. 3 presents results of X-ray phase analysis of $C_{petroleum.coke}$ – TiC/TiB_2 composite, synthesized at 1050ºC with initial composition[13] of $C+26(Ti+B_2O_3)$. As expected, the main phase with maximum intensity represents carbon. Target phases with less intensity are represented by titanium and boron compounds, synthesized by titanium borides and carbides TiB_2, TiB, TiC_x according to overall reaction (4):

$$2Ti + B_2O_3 + 4C \rightarrow TiB_2 + TiC + 3CO \qquad \Delta G^0_{1300} = -215{,}63\ \text{kJ/mol} \tag{4}$$

The detected titanium borate $TiBO_3$ and titanium oxide TiO_2 are products of partial oxidation of titanium borides during the process of electrodes synthesis.

The definition of relative electrodes stability in air atmosphere was carried out in muffle furnace with possibility of automatic heating with the rate of 300°/h and holding time of 5 hours at 520, 710, 820, 920 and 1050ºC. The duration of cyclic tests was up to 30 hours (heating – holding during 5 hours – cooling).

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[13] Here and further compositions of initial composite charge are given in mass percentage.

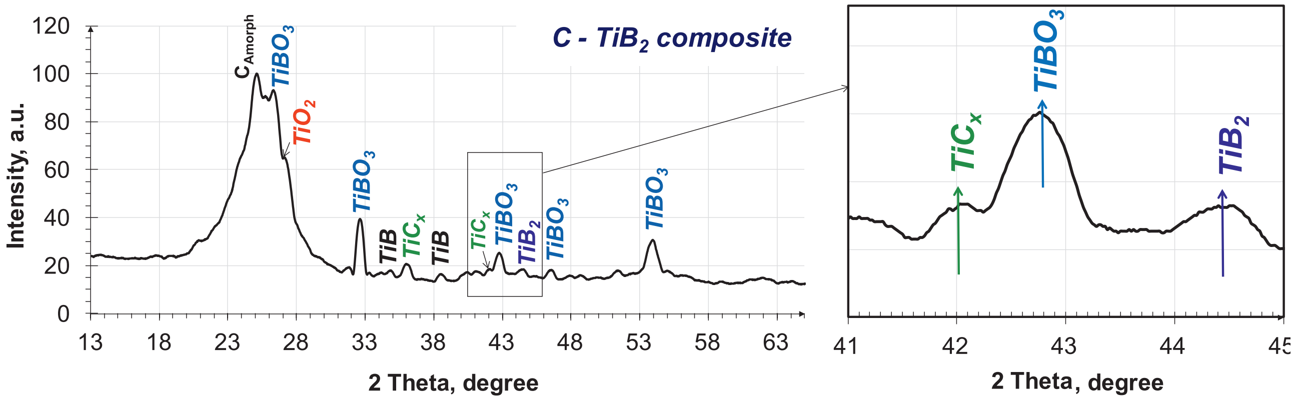

Fig. 3. *Results of X-ray phase analysis of the composite after the synthesis with initial composition of C+26%(Ti+B_2O_3)*
Рис. 3. *Результаты РФА композита после синтеза с исходным составом С+26%(Ti+B_2O_3)*

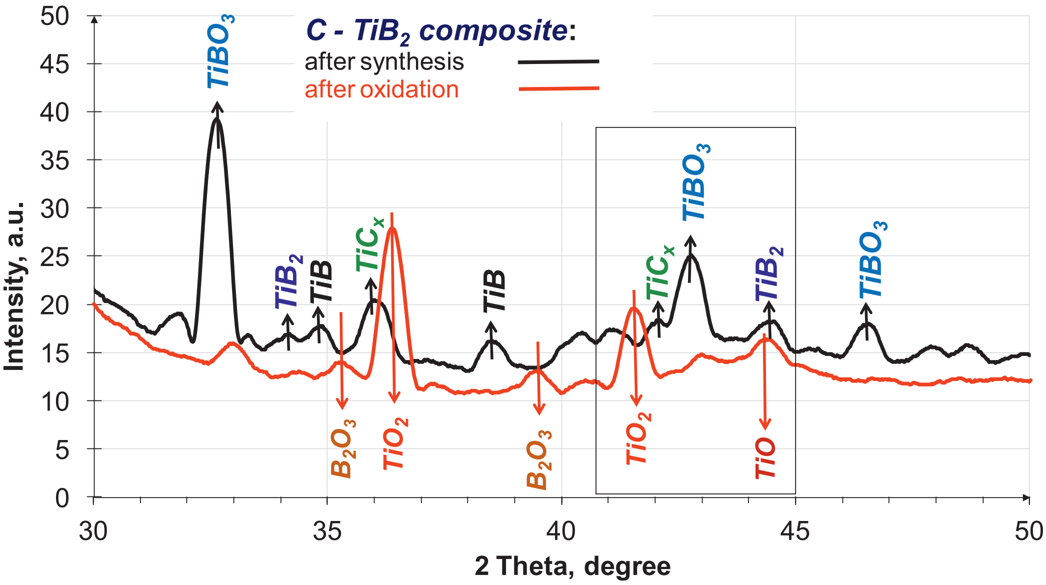

Fig. 4. *X-ray phase analysis results of C + 26(Ti+B_2O_3) composite after synthesis and consequent 30-hour oxidation at 710°C in air atmosphere*
Рис. 4. *Результаты РФА композита С + 26(Ti+B_2O_3) после синтеза и окисления в течение 30 ч при 710°C в атмосфере воздуха*

During this period of oxidation carbide and boride phases of titanium are transformed on the surface into its oxides TiO and TiO_2 forming glass phase B_2O_3 (Fig. 4 and 5). It means, liquid boron oxide forms a continuous layer, wetting a composite base of material, partially oxidized, and an initial carbo-boride structure of polycrystalline product.

Till 1000ºC the oxidation rate of composite specimens keeps the downward dynamics with passive character of oxidation, and it is described by equations of power dependence (Fig. 6). This could mean that the process depends not only on the stability of oxi-carbo-boride bond of the composite, but also on the supply (diffusion) of oxygen through the increasing layer of boron oxide glass phase on the surface of pore space through the growing layer of titanium oxides. It means in this mode the losses of electrode mass depend on mixed mode of diffusion and interaction of oxygen with electrode base.

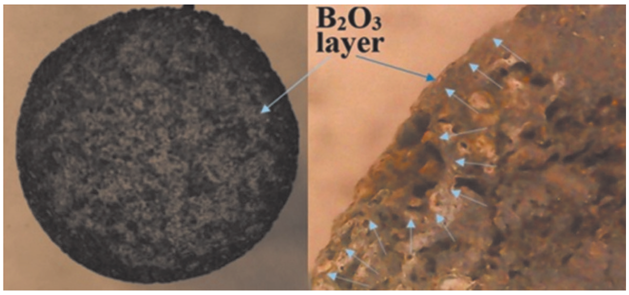

Fig. 5. *B_2O_3 glass phase layer on the composite specimen surface after its oxidation at 710°C*
Рис. 5. *Слой стеклофазы B_2O_3 на поверхности композита после окисления при 710ºС*

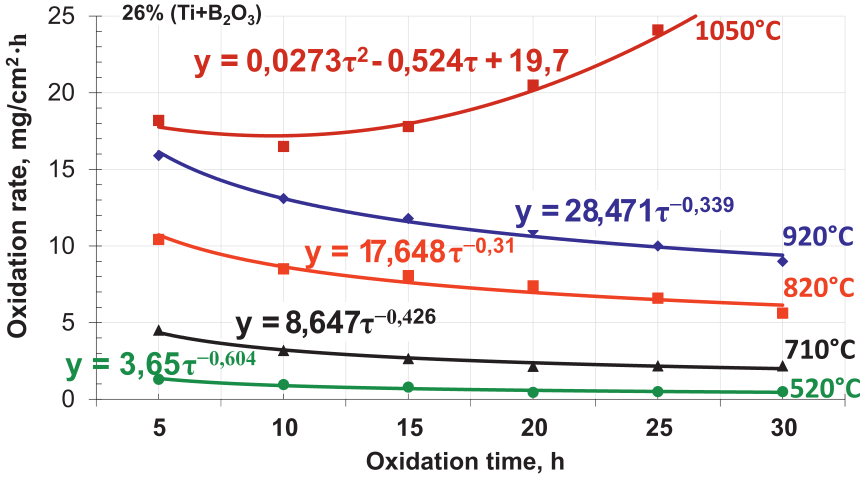

Fig. 6. *Oxidation rate of composite electrodes with initial composition of C+26%(Ti+B_2O_3) in the temperature range from 520°C to1050°C in air atmosphere*

Рис. 6. *Скорость окисления композитных электродов с исходным составом C+26%(Ti+B_2O_3) в температурном интервале 520–1050°C в атмосфере воздуха*

If exceeding 1000ºC, in our case at 1050ºC, the initial oxidation rate reduction is changed to active oxidation character because of B_2O_3 evaporation. Under these conditions the oxidation rate increases with every subsequent cycle and it is described by polynomial equation (Fig. 6). This means that in steady-state mode the material oxidation depends on direct interaction of oxygen with carbon.

So, with simplicity of adapting the $C_{petrcoke}$ – TiC/TiB_2 technology to industrial conditions of mixing, pressing, and baking at 1000–1100°C the enhanced resistance of electrodes to the oxidizability with atmospheric oxygen is achieved. The presence of refractory compounds in carbon composites supposes their less susceptibility to different types of wear and to the impact of alkali metals and acquisition of the property of wettability with liquid metals. These potential operating properties shall be defined during further investigations.

Composite electrodes, based on natural graphite[14]. The development of the material for specimens of C_{graph} – TiC/TiB_2 electrodes, based on natural graphite GL-2 was carried out by its preliminary oxidation and intercalation with oleum in the presence of nitric acid or potassium permanganate according to well-known methods [102, 103]. Modification of graphite intercalation compounds was fulfilled by introducing titanium and boron ions, being part of the composition of titanium sulphate $Ti_2(SO_4)_3$ and boric acid H_3BO_3 solutions directly into the oxidizing composition.

After washing and drying oxidized and modified graphite was exposed to the thermal shock at the temperature of 850°C for 5–15 min. Parameters of graphite oxidation, modification and thermal treatment were selected in such a way to minimize the degree of thermal expansion in order to provide an workable specimen compacting. The shape and structure of thermally expanded graphite (TEG) particles changed from initial laminar to foam-dendritic thermally treated material (Fig. 7). At the same time the particle size distribution remained in the range of 50–250 mcm, but the balk density of material changed considerably from 0.45–0.47 to 0.040–0.042 g/cm³.

The specific electrical resistivity of the powders of initial (~66000 μΩ·m) and thermally expanded (~6700 μΩ·m) graphites differed by an order of magnitude[15], but with the increase

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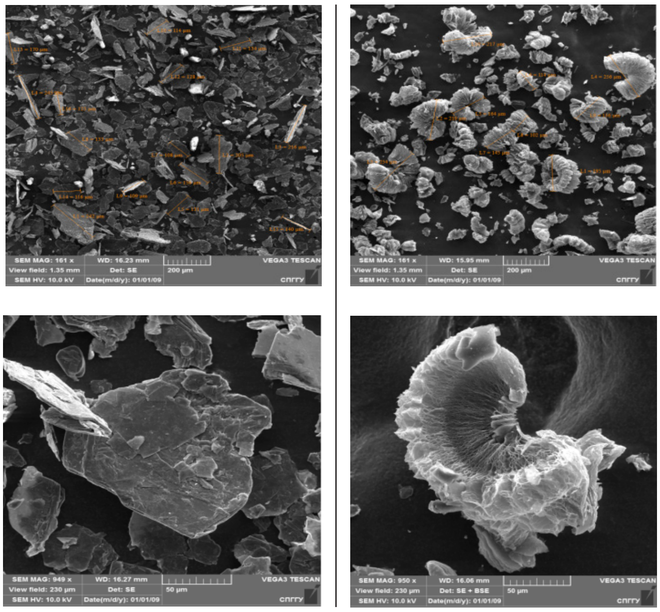
[14] Perspectives of using natural graphite for the production of electrodes are opened due to the plans of LLC "Dalgraphite" (being part of LLC "Magnesite Group") to produce annually 40.5 thousand tons of graphite concentrate. Available from: https://dalgraphite.ru/ [Accessed 7th June 2024].

[15] The measurement of specific electrical resistivity of powders and compact carbon materials was carried out in accordance with GOST 23776-79 "Methods for the measurement of specific electrical resistivity".



a b

Fig. 7. Microstructure of initial (a) and thermally expanded (b) natural graphite
Рис. 7. Микроструктура природного графита исходного (a) и терморасширенного (b)

of powder compaction degree this difference reduced[16].

However, at the compaction degree of 1.9 the difference in electrical resistivity of graphites remained significant – 7 times higher (Fig. 8). In that respect it should be assumed that this trend in the ratio of electrical resistivity for graphite compact specimens would be sustained, i.e. the electrical conductivity of graphite products made of TEG powders, would increase.

To develop C_{graph} – TiC/TiB_2 electrodes the standard laboratory procedure of mixing initial materials, their pressing and baking was used, similar to the fabrication of $C_{petrcoke}$ – TiC/TiB_2 electrodes. At the same time components of graphite oxidation-intercalation, concentration of modifying liquors ($Ti_2(SO_4)_3$ + H_3BO_3) and thermal shock parameters were varied for different specimens.

The definition of relative C_{graph} – TiC/TiB_2 electrodes stability in air atmosphere was

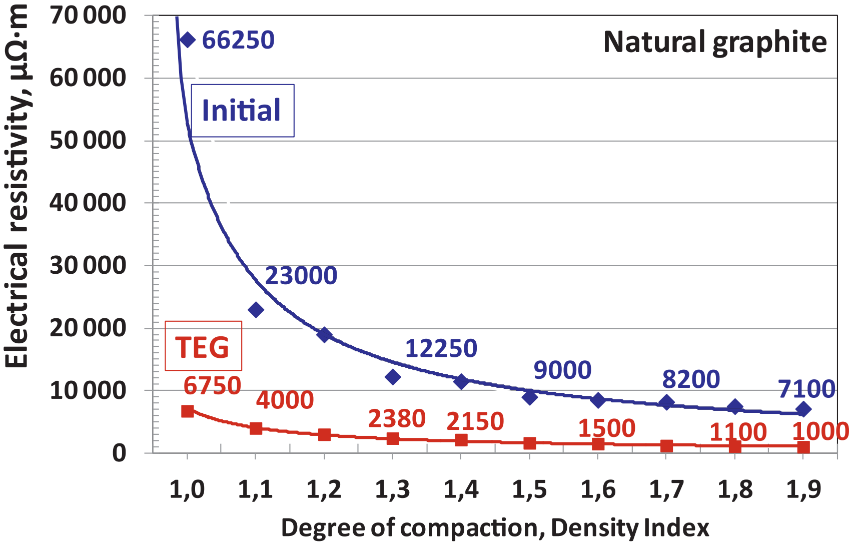


Fig. 8. Specific electrical resistivity of the initial and thermally expanded graphite
Рис. 8. Удельное электросопротивление исходного и терморасширенного графита

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[16] Compaction degree is the ratio of current density of the powder to its initial bulk density.

carried out at 710ºC in comparison with the definition of oxidizability of electrodes made of initial natural graphite. Electrode specimens of 1–4 differ from each other by conditions of their preliminary treatment for baking process – synthesis (Fig. 9). The duration of cyclic tests was up to 30 hours (heating – holding during 5 hours – cooling).

Obtained results give evidence of high potential development of composite C_{graph} – TiC/TiB_2 electrodes for ore thermal furnaces, magnesium and aluminium cells that would have a high stability in oxidizing environment. Preliminary intercalation of the structure and modification of natural graphite composition with subsequent destruction of the material at the thermal shock supposes the production of the goods with high electrical conductivity, resistance to wear and penetrated components (Na, K, $FeCl_3$, $AlCl_3$, Cl_2, F…). Particular features of the C_{graph} – TiC/TiB_2, technology, besides the preliminary procedure of initial graphite structure destruction, are minimization of binding agent for the compaction, no need for

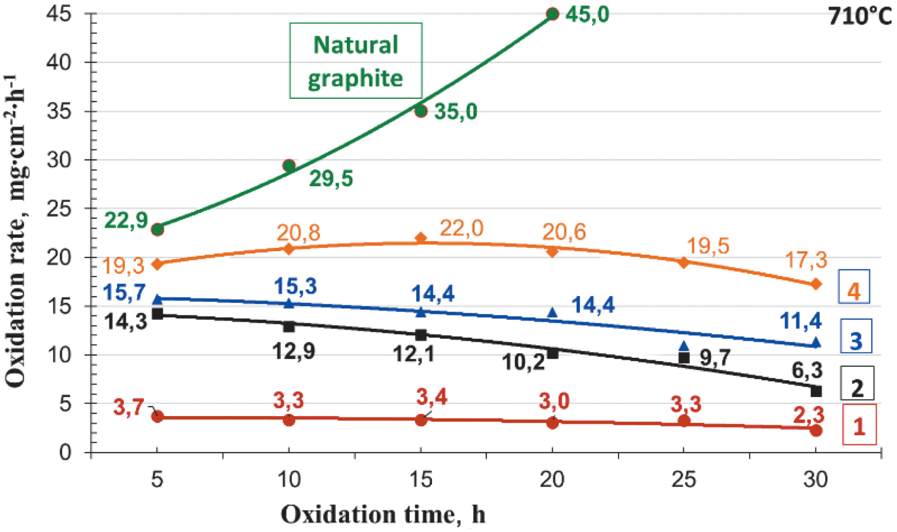

Fig. 9. *Oxidation rate of C_{graph} – TiC/TiB_2 composite electrodes of various compositions 1–4 at the temperature of 710°C in air atmosphere*
Рис. 9. *Скорость окисления композитных электродов C_{graph} – TiC/TiB_2 различных составов 1–4 при температуре 710°C в атмосфере воздуха*

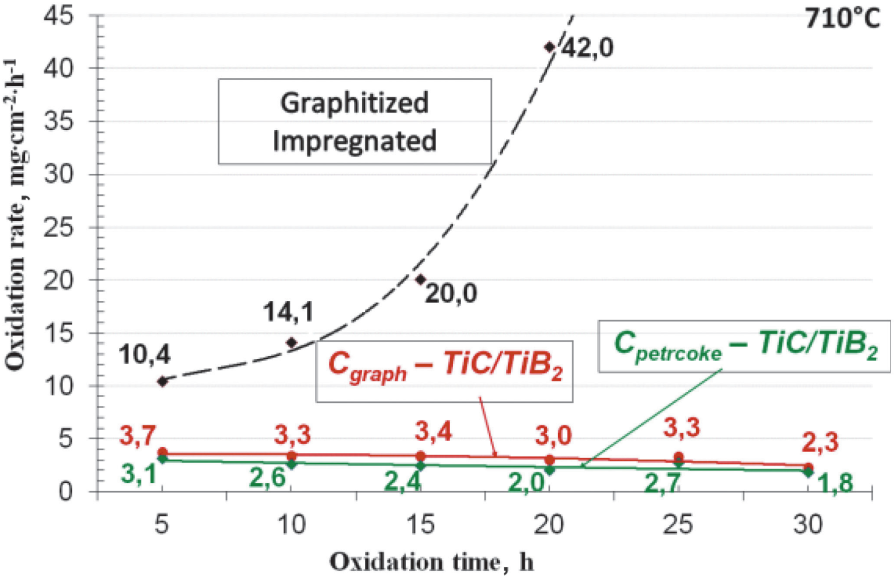

Fig. 10. *Comparative oxidation rate of composite and graphitized electrodes at the temperature of 710°C in air atmosphere*
Рис. 10. *Сравнительная скорость окисления композитных и графитированных электродов при температуре 710°C в атмосфере воздуха*

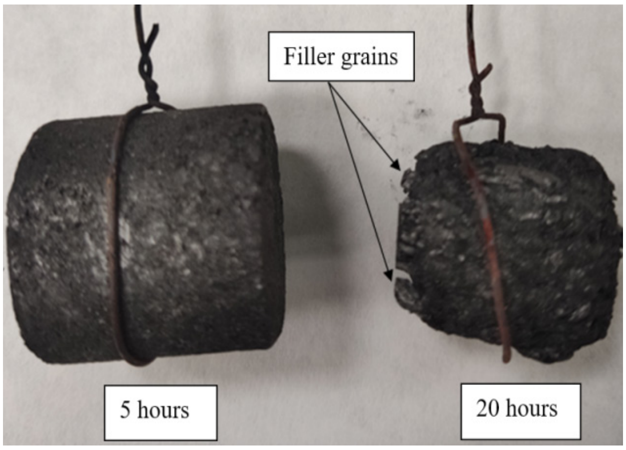

Fig. 11. *Graphitized specimens impregnated with a protective composition after 20-hour oxidation at the temperature of 710°C in air atmosphere*
Рис. 11. *Внешний вид графитированных образцов, пропитанных защитным составом, после 20 ч окисления при температуре 710°C в атмосфере воздуха*

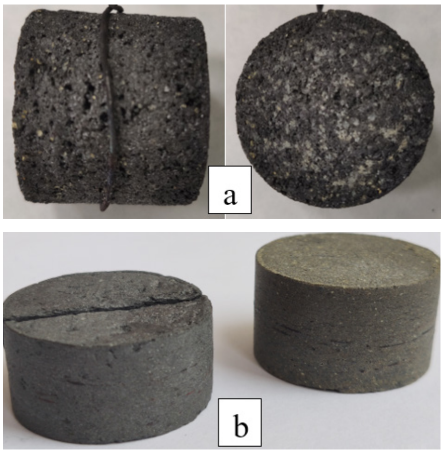

Fig. 12. *$C_{petrcoke}$ – TiC/TiB$_2$ (a) and C_{graph} – TiC/TiB$_2$ (b) composite specimens after 30-hour oxidation at the temperature of 710°C in air atmosphere*
Рис. 12. *Внешний вид композитных образцов $C_{petrcoke}$ – TiC/TiB$_2$ (a) и C_{graph} – TiC/TiB$_2$ (b) после 30 ч окисления при температуре 710°C в атмосфере воздуха*

needle coke application and its graphitization for the production of electrodes of specific quality.

Advantages of composite $C_{petrcoke}$ – *TiC/TiB$_2$* and C_{graph} – *TiC/TiB$_2$* electrodes vs electrodes of natural graphite and graphitized electrodes impregnated with protective solutions are evident. And this is evident not only in graphs of the rate of mass loss (Fig. 9 and 10), but also in appearance (Fig. 11 and 12).

Results, obtained in laboratory conditions, are intermediate in current investigations and these investigations shall continue during the tests in conditions of electrolytic reduction of fluoride and chloride melts.

CONCLUSIONS

1. Based on literature review it is established that carbon-graphite products for ore thermal furnaces, magnesium and aluminium cells are subjected to the high-temperature oxidation, wear and influence of interlayer compounds.

2. Reactive capability of poly-crystalline carbon material in regards to gas oxidizing agents depends on structure perfection degree, size of crystallites and presence of impurities.

3. Losses of the electrodes due to the oxidation of their side surface in electrical arc furnaces, when they pass through the temperature zone of 600–800ºC, achieve 40–60% from their total consumption.

4. Significant destructive effect is exerted on carbon-graphite electrodes by specific interaction of carbon with elements and compounds from working environment, which are capable to penetrate (intercalate) into the interlayer carbon structure. The destructive interaction with sodium and potassium occurs in carbon-graphite cathodes of aluminium cells at the temperatures lower than 850°C forming $C_n^-K^+ \cdot 2K, C_n^-Na^+ \cdot 2Na$. Under cyclic changes in temperature field the interaction carbon – Na/K results in abnormal (low-temperature) graphitization of cathode block material.

- Graphite anodes of magnesium cells are subjected to the destruction at the interaction with chlorides of copper, iron, manganese, aluminium and at the formation of interlayer compounds like $C_n^+Cl^- \cdot 3AlCl_3$, $C_n^+Cl^- \cdot FeCl_2 \cdot 3FeCl_3$ under temperatures of 200–300°C. Under temperatures, exceeding 600°C graphite anodes are stable.

5. The protection of electrodes for electric arc furnaces and anodes for magnesium and aluminium cells is carried out by thorough sealing, by applying to the side surface the solutions, inhibiting the oxidation, or coatings with physical and chemical nature of action:

- Water solutions of orthophosphoric and boron acids.
- Mixtures of zinc ($Zn(H_2PO_4)_2 \cdot 2H_2O$) and aluminium ($Al(H_2PO_4)_3 \cdot 2H_2O$) phosphates in orthophosphoric acid.

- Ceramic coatings based on oxides Al_2O_3, SiO_2, B_2O_3, TiO_2, carbides SiC and B_4C, or on complex compounds like ZrB_2–SiC–$TaSi_2$–Si.

6. Proposed and available technical solutions for the protection of the surface of carbon products have not been widely recognized or are not in use in metallurgical branch. The probable cause consists in the limited electrode protection period, complexity of their implementation or lack of profitability due to the high cost of protective components.

7. The promising direction to produce corrosion resistant materials is proposed – synthesis of composite C – TiC/TiB_2 electrodes, based on petroleum coke and graphite in standard conditions of industrial production.

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