The use of titanium diboride to protect the cathodes of aluminum electrolysis cells

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Abstract. The analysis of modern technical solutions for the protection of the cathodes of electrolysis cell was carried out. The technological variant of obtaining protective coatings based on nanocrystalline titanium diboride is substantiated and proposed. A comparison of the basic and expected indicators of aluminum production is made using cathodes with protective coatings. A technical solution has been developed to organize the production of nanocrystalline titanium diboride. Its main technical and economic indicators are substantiated.

1. Introduction

Modern metallurgy provides the world economic system with a variety of metal products of both mass and special purposes. According to the World Steel Association, in the structure of metal products consumption 94% is accounted for iron alloys and non-ferrous metals – 5%, 1% is made up of a diverse group of metal-containing materials with a special set of properties.

An important place in this group is occupied by borides of metals of subgroups of titanium, vanadium and chromium, materials and alloys based on them, which, thanks to a unique combination of practically significant properties, are used in machine, aircraft and rocket science to solve applied engineering, technical and production problems requiring high temperature, superhard, heat-resistant, heat-resistant, wear-resistant structural, refractory, surfacing materials and protective coatings capable of working in extreme conditions.

This group includes titanium diboride TiB₂, investigated and put into circulation by the scientific school of the famous Russian material scientist G.V. Samsonov more than 50 years ago and still in demand. At the same time, applied interest in the production and use of titanium diboride is constantly growing and reflects the trend of the transition from the use of coarse-grained titanium diboride to micro- and nanocrystalline. This is due to the desire of scientists and technologists-practitioners to achieve a qualitatively new level of operational properties of materials and coatings based on it.

In this regard, the study and technological implementation of boride formation processes during the plasma metallurgical processing of titanium-boron-containing raw materials is an important scientific and practical task of great importance for the development of domestic titanium metallurgy and its multifunctional compounds, as well as the effective solution of innovative problems of applied materials science.
2. Wetted coating materials for cathodes of electrolysis cells

Aluminum alloys are widely used in many engineering industries due to their low density and relatively high strength. The world production of primary aluminum is constantly growing, currently reaching a volume of about 47 million tonnes/year [1]. Commercial aluminum is obtained by electrolysis of a fluoride cryolite-alumina melt containing dissolved alumina $\text{Al}_2\text{O}_3$ at a temperature of 1213-1243 K.

The process is implemented in horizontal cells with carbon graphite anodes and cathodes. At the same time, molten aluminum is the real cathode in the electrolytic baths, under whose layer there is a carbon-graphite lining with a life of 5-8 years. The main disadvantage of such a hearth is the non-wettability of molten aluminum. Therefore, between the bottom and liquid aluminum, a thin layer of electrolyte accumulates, which facilitates the penetration of sodium into the crystal lattice of the carbon-containing materials of the bottom and its destruction.

In this regard, over the past 20 years, the volume of research and technological proposals has been expanding in world practice aimed at selection of materials for cathode lining, formation of wettable coatings on it, or manufacturing bulk products of its components [1-6].

The cathode material must satisfy a number of requirements, namely, it must be resistant to molten aluminum and electrolyte, highly conductive, strong enough, wetted by aluminum melt well (i.e., have high adhesion to it), and its linear wear rate should not exceed 3-5 mm per year. Such a set of properties can be realized only in a composite material having a functional basis and phase additives that perform various purposes. According to [2], borides and carbides of refractory metals can be used as part of a functional framework.

Currently, titanium diboride $\text{TiB}_2$ is recognized as the most effective functional material for wettable cathodes of cells. This is confirmed by the results of large-scale industrial experiments conducted at different times by the Great Lakes companies, Reynolds Metal (USA), Komalko (Australia), Shenyang Sheng IED (China) [2]. Various options for cathodic coatings were studied: hot-pressed tiles made of $\text{TiB}_2$, a composite coating with a binder ($\text{TiB}_2 + \text{graphite powder} + \text{resin/pitch}$; 30-60% $\text{TiB}_2$ + 40-60% anthracite + 5-20% graphite powder + 5-20% pitch; $\text{TiB}_2$ + resin/pitch, $\text{TiB}_2$ + $\text{Al}_2\text{O}_3 + \text{H}_2\text{O}$). Coatings were applied to the hearth with tile lining, pouring and compaction with vibration, spraying, staining.

In all cases, there is a decrease in the cathodic voltage drop (up to 15-30 mV), an increase in current efficiency (by 1-2%), an improvement in the stability of the cell energy parameters, a decrease in damage to the cathode blocks, and the possibility of reducing the interpolar distance (by about 1 cm), technological preference for the use of $\text{TiB}_2$ + binder. Indeed, insufficient heat resistance, the cost of manufacturing monolithic products and, most importantly, the high cost of marketable diboride powder allow it to be used only in composites. The proposed thin coatings based on $\text{TiB}_2$ wear out quickly and are therefore ineffective, and thick coatings or bulk products are economically disadvantageous even with a diboride content reduced to 30-40%. An even lower content does not provide reliable wetting of the composite with aluminum. Partially, these shortcomings are eliminated by the use of unsintered heterophase powder composites based on $\text{TiB}_2$ with fillers, which should also be resistant to liquid aluminum (as a rule, various forms of carbon, as well as corundum). A carbon or alumina binder during heat treatment in the manufacture of cathode products fastens the phase components of the material into a monolithic solid, forming a composite, the wettability of which is achieved by aluminum due to a certain volume content of $\text{TiB}_2$.

In [7], one of the technological options for the preparation and use of a coating based on $\text{TiB}_2$ wetted by aluminum was described. To obtain such a coating, an aqueous suspension is prepared containing 68-70% solid (90% $\text{TiB}_2$, 10% $\text{Al}_2\text{O}_3$). The physical and chemical bond between colloidal $\text{Al}_2\text{O}_3$ particles and $\text{TiB}_2$ particles in suspension leads to the formation of a viscoelastic, jelly-like state of the material. Such material does not emit water and behaves as a solid after drying.

The suspension is applied by spraying or staining with intermediate drying by air after applying each layer. The total drying time is 24 hours. A coating with a thickness of 1.0-2.0 mm provides wetting of the cathode with aluminum, has a high resistance to sodium penetration, at the same time
combines sufficient hardness, bending strength, wear resistance, adhesion to the base, helps to reduce the cathodic voltage drop and increase the cathode current output of aluminum.

Thus, TiB₂ coating cathode protection is a powerful reserve of energy saving in modern aluminum production, estimated at 10%. This indicates the need for further development of the technological base of its production. The main methods for producing TiB₂ for wettable cathode coatings are self-propagating high-temperature and furnace synthesis. However, these methods, with the relative simplicity of the technological solution, are inefficient and make it possible to obtain TiB₂ in the form of a sufficiently large powder with particles in the size range of 5–10 μm. There is reason to believe that the introduction of TiB₂ into the suspension in the form of a finer powder with a particle size smaller or comparable with the particle size of Al₂O₃ (0.1 – 1 μm) will enhance the physicomechanical and protective properties of the coating.

3. Protective coatings of cell cathodes
In the foreign practice of aluminum production, materials for protective cathode coatings of cells are supplied by MOLTEK company and have the TINOR A, TINOR M trademarks and thickened TINOR [2]. RUSAL also shows a certain technological interest in the creation and industrial use of wettable cathodes. In 2016, its Engineering and Technology Center, together with Energoprom Group, the largest Russian producer of carbon-graphite materials, began production tests of cells with protective coatings of cathodes based on the TiB₂ + pitch composition in the conditions of RUSAL-Krasnoyarsk JSC. In this regard, an assessment of the prospects for the development and implementation of a wettable cathode technology within the company was made, some results of which are shown in table 1.

The assessment was carried out for the conditions of 2016 from the assumption of a decrease in the interpolar distance by 1 cm, an increase in the cathodic aluminum current output by 1%, a decrease in the voltage drop in the aluminum-hearth contact by 50 mV, a coating thickness of 8 mm, and a specific TiB₂ consumption of 0.26 kg/t Al, an increase in the average life of the cell from 1625 to 2555 days with a unit cost of overhaul of 2500 rubles/t Al.

The annual demand in titanium diboride at one aluminum plant, for example, Khakassky with one extra-long series of electrolysis with a voltage 1600 V, current 350 kA, 336 installed cells with capacity 280 000 tonnes of aluminum per year, is 72 tonnes.

A technical proposal has been developed for aluminum-producing enterprises to organize their own production of nanocrystalline titanium diboride as the main component of the cathode coatings of aluminum electrolysis cells, including the technological process for producing titanium diboride, a complex of basic and auxiliary equipment, and substantiation of the main technical and economic indicators of production. The hardware-technological scheme for producing nanocrystalline titanium diboride is shown in figure 1.

Table 1. Basic and expected indicators of aluminum production by RUSAL (Russia) with the use of cathodes UG and UG - TiB₂.

| Indicators of aluminum production          | UG cathodes | UG - TiB₂ cathodes |
|-------------------------------------------|-------------|--------------------|
| Production Al, t/year                     | 3724000     | 3724000            |
| Specific power consumption, kW·h/t Al    | 14000       | 12500              |
| Energy loss reduction, kW·h/t Al         | -           | 1500               |
| Annual energy consumption, kW·h/t Al     | 521760000000| 46550000000       |
| Energy saving, kW·h/t                    | -           | 5586000000        |
| Monetary savings, $/year                 | -           | 123203000         |
| Equivalent production Al, t/year         | -           | 44700              |
| Average cathode life, day                | 1625        | 2555               |
| Unit repair costs, rub/t Al              | 2500        | 2500               |
| Monetary savings, $/year                 | -           | 99306000          |
| Total cost in terms of money, $/year     | -           | 225120000          |
Specific consumption $\text{TiB}_2$, kg/t Al - 0.26
Need in $\text{TiB}_2$, t/year - 968
Reasonable price $\text{TiB}_2$, $/kg - 230

Figure 1. Process flow diagram for producing nanocrystalline titanium diboride: 1 – storage of charge materials and charge preparation; 2 – dosing; 3 – mixing; 4 – drying; 5 – rubbing; 6 – loading the charge into the dispenser; 7 – plasma treatment; 8–9 – cooling of the exhaust dust and gas flow and separation of the target product; 10 – collection, quality control and packaging.

The required investment for organizing the production of nanocrystalline titanium diboride in 3 plasma-metallurgical reactors with a total capacity of 450 kW is 93.3 million rubles. The annual demand for raw materials is PTN-8 grade titanium powder 37.3 t/year, B-99 grade boron powder 17.1 t/year, energy consumption – 2.06 million kWh/year. At the same time, annual production of 52 tonnes/year is forecasted at a selling price of 34,670 rubles/kg. The payback period for capital investments is 0.5 years.

4. Conclusion
The technical proposal for aluminum-producing enterprises concerning the organization of nanocrystalline titanium diboride production was developed, which is component of the cathode protective coatings of aluminum electrolysis cells, including the technological process, basic and auxiliary equipment, and substantiation of the main technical and economic indicators of production. The required investment with an installed capacity of 450 kW is 93.3 million rubles. It is projected to achieve annual output of 52 tonnes/year, selling price of 34,670 rubles/kg, a payback period of investment of half a year.

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