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To cite this article: S N Fedorov and P S Palyanitsin 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **560** 012180

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Energy efficiency in primary aluminium industry

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Abstract. The extraction of metals and subsequent processing into finished product takes place in series of various operations which demand the usage of much energy. Saving energy is the main purpose of the present industry investigations. Aluminium industry is one the greatest energy consumers with 13-17 kWh/kg of Al and low energy efficiency of 40-50 %. At the same time every day researchers strive to increase current output and reduce energy consumption of aluminium pots for primary aluminium used in various applications. In the present work, the attention is given to the energy efficiency. In particular, it is considered that titanium diboride is used in cathode pot lining to prolong cell's life cycle, to reduce the electric consumption of cell series due to the voltage drop and reducing anode to cathode distance.

1. Introduction

The extraction of metals and subsequent processing into a finished product takes place in the series of various operations. The extraction and production will surely cause some degree of environmental disturbance. Aluminium industry is not an exception as it is being produced by the Hall-Heroult process [1]. Moreover, the primary aluminium producing process consumes much energy with 13-17 kWh/kg of Al and 40-50 % energy efficiency [2-4]. It is also most negatively impacting the environment factor due to its complexity, the need for fluoride compounds' usage, as well as the periodic complete replacement of the pot lining. At the same time researchers daily strive to maximize the positive environmental contribution of aluminium used in various applications [5, 6]. In the present work, the attention is given to the ways of decreasing of the aluminium pot's energy consumption.

The cathode device is a cell that is based on carbon-graphite blocks (figure 1). There is a refractory and heat-insulating lining between the walls of the casing and the blocks. Specially manufactured structural materials of the bottom are resistant to the aggressive action of molten electrolyte [3-6]. The most important part of cathode lining is cathode blocks that have to be highly electrically conductive, inert to interaction of smelt and to have high mechanical hardness. Titanium diboride is a more promising material to upgrade cathode blocks. This allows one to prolong cell's life cycle, reduce electric consumption of cell series thanks to reducing in voltage drop and cutting down anode to cathode distance.



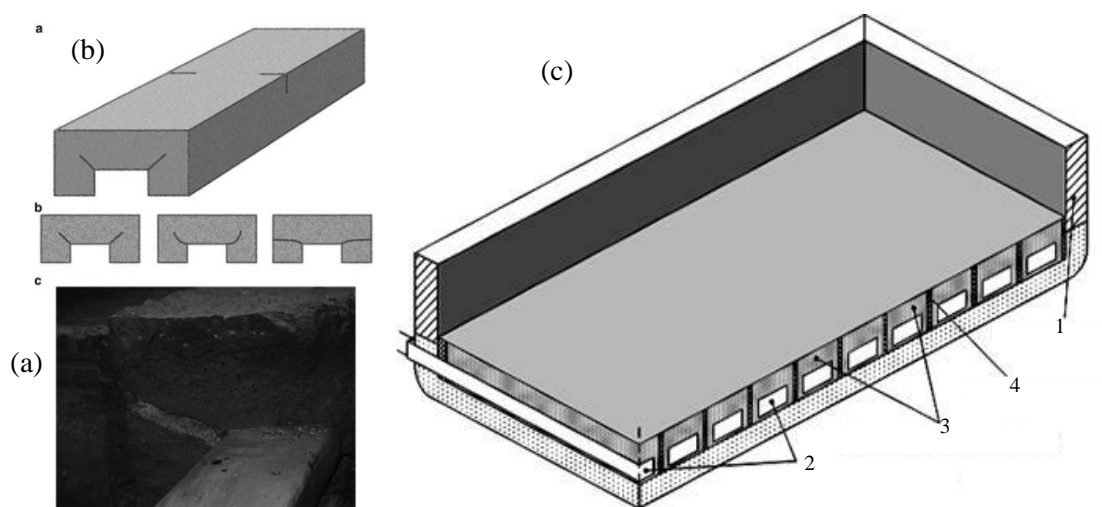


Figure 1. Industrial cathode blocks (a), draw (b) and aluminium cell (c) (1 – pot (steel casing and brick lining), 2 – cathode rods, 3 – graphite cathode blocks, 4 – stuffed seams).

Titanium diboride possesses a number of important properties, which determines its significance:

- high hardness;
- significant refractoriness;
- increased resistance to abrasive wear;
- neutron-absorbing properties.

Therefore, titanium diboride is used in various industries, such as machine building, in metallurgy as a wear-resistant component of surfacing materials and powder for spraying, to protect the surfaces of machines and friction surfaces of machine parts from abrasive wear by plasma spraying, for evaporators of aluminum, also in nuclear power engineering as a neutron absorber its material [3-6].

The investigations of titanium diboride used into cathode lining were started in 1955 by R. A. Lewis [7], and are still conducted these days [8-10]. But the problem is in the cost of the material that limits its usage. There have been many investigations of titanium compounds' production, but the conditions of manufacturing, final characteristics of the material are not suitable for final consumers [11-15].

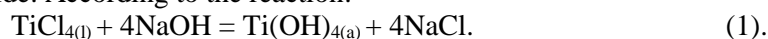
2. Experimental method

The present studies of the features and prospects of the synthesis of refractory compounds in the Ti-B-O-C system have been undertaken to remove the economic limitations of the widespread use of titanium borides in the metallurgical industry. It is assumed that the use of inexpensive and inexpensive starting components for their production in low-temperature conditions up to 1070 °C using simple equipment will significantly reduce the cost of these powders to the level of commercial use. Such compounds are titanium and boron oxides in the hydrated form of $\text{Ti}(\text{OH})_{4(a)}$ and boric ($\text{H}_3\text{BO}_3 = 1/2\text{B}_2\text{O}_3 \cdot 3/2\text{H}_2\text{O}$) acids, which allow using "wet" methods of mixing reagents to increase the reaction surface, in particular sol-gel technology.

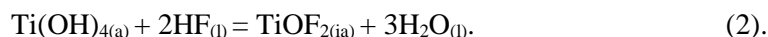
There are three main studies of how to synthesize the titanium diboride:

- 1) mixture preparation including calculating stoichiometric chemical reactions rates;
- 2) modifying TiO_2 for stabilization anatase form until 1000 °C;
- 3) synthesis of TiB_2 using different atmospheres (argon, vacuum, high pressure).

The preparation of the reaction mixture involves the hydrolysis of titanium tetrachloride for producing fresh hydrated titanium oxide. According to the reaction:



Then after fluorination from hydrofluoric acid, there is the modified titanium dioxide in the aqueous medium:



After doping the original amorphous titanium oxide into its gel-like solution $\text{TiOF}_{2(\text{ia})}$, the remaining components of the reaction mixture (boric acid and carbon in the form of sucrose) were successfully added to a molar ratio of $\text{TiO}_2\text{:B}_2\text{O}_3\text{:C}$ under the constant stirring. The resulting mixture was dried at room temperature, then in a drying oven - at the temperature of 80-90 °C. The obtained agglomerated $\text{TiO}_2\text{-B}_2\text{O}_3\text{-C}$ composite was heated in a water-cooled sealed cell with the possibility of adjusting the gaseous atmosphere:



The mixture of the reaction was heated to the temperature of 800-1000 °C in air atmosphere for saving the anatase form of the dioxide titanium. When the temperature reached 800-1000 °C, a vacuum was installed in the system. Afterwards the 1-3kPa vacuum was established for 3-4 hours when the temperature achieved 1050 °C. The synthesis can be called "low temperature" because usually 1700-2000 °C were used in the industry to produce titanium diboride [13-14].

After the end of exposure at the fixed temperature and the completion of low-temperature synthesis, the samples were extracted from the reaction zone, weighed and directed to X-ray phase analysis of XRD ($\text{CuK}\alpha$).

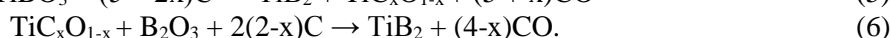
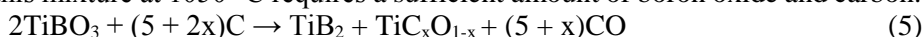
3. Results and discussions

First of all, it is necessary to verify the possibility of reducing the doped titanium oxide with carbon and determine the order and depth of phase formation when the reaction mixture is heated to 1050 °C.

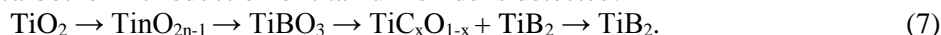
In a general form and as a mixture, these two parallel processes can be represented as follows:



Further reduction of this mixture at 1050 °C requires a sufficient amount of boron oxide and carbon:



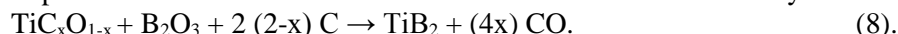
With shortage of these compounds, the titanium oxycarbide with an admixture of titanium diboride TiB_2 was obtained in the discussed experiments. Thus, according to the results of the studies, the following sequence of carbothermic reduction of titanium oxide is detected:



XRD analysis shows that the obtained samples after 4 hours of soaking at 1050 °C in vacuum and in the atmosphere of inert gas (argon) contain different titanium compounds (Figure 2). Argon atmosphere allows one to get titanium oxyboride with an admixture of titanium diboride TiB_2 . Titanium diboride can be produced in vacuum with more than 90 % wt.

Synthesis of the $\text{TiO}_2\text{-B}_2\text{O}_3\text{-C}$ mixture in an argon atmosphere at 1050 °C produced titanium diboride-titanium borate with traces of titanium oxides, which is due to the presence of oxygen in an inert gas.

The experiment in vacuum produced titanium diboride with traces of unreduced titanium oxycarbide:



We noted that in this case, as in all other experiments, the B_2O_3 phase in the synthesis products was not detected. This gives grounds to assume that at temperatures above 1000 °C, boron oxide liquid is subject to gasification. In this connection, subsequent studies should be directed to a study of the mechanism for obtaining the target condensed phases.

There are several ways to achieve suitable phases. In case of producing titanium diboride, it is needed to set airtight atmosphere with 1-3 kPa which then can be used into cathode blocks.

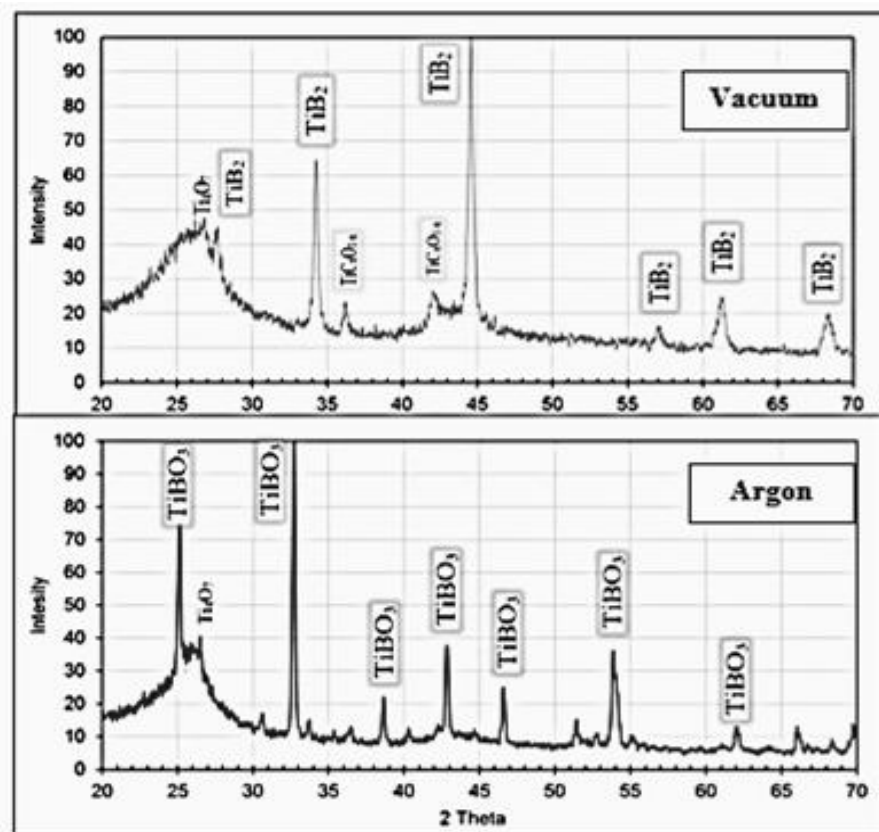


Figure 2. XRD analyze of the obtained samples after 4 hours of soaking at 1050 °C.

Afterwards, the obtained titanium diboride is being grinded into powder with a dominant fraction of 10 μm , which is 5-10 times smaller than the carbon graphite material that is used for the cathode blocks. This operation makes it possible to have a large specific surface area, thereby minimizes the electrical resistance of the future cathode. Carbon-graphite cathode blocks with a content of 15 % by wt. and 30 % wt. of titanium diboride were used in a laboratory plant as a cathode (Figure 3). The cryolite-alumina melt had a cryolite ratio of 2.5, the temperature of the process was 960 °C, and the current intensity was 20 A. In addition to the change in electrical conductivity, which was higher on samples with titanium diboride, it was found that the modified blocks were wetted with aluminum.

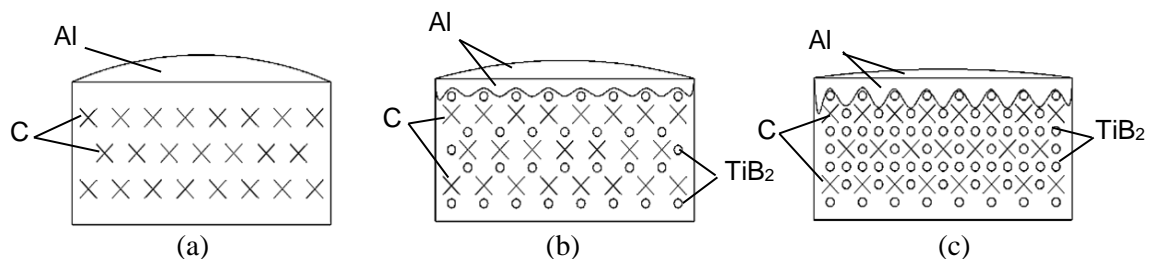


Figure 3. Cathode blocks: (a) carbon-graphite only, (b) carbon-graphite with 15 % wt. TiB_2 , (c) carbon-graphite with 30 % wt. TiB_2 .

Anode to cathode distance can be reduced significantly due to aluminum's wetting effects. The proposed design of the cathode device of an aluminum pot provides the following industrial process of producing aluminum:

- 1) decrease in the rate of circulating flows of cathode metal;

2) reduction of the negative magnetic field for the process of interaction with horizontal currents in the metal;

3) improvement of current distribution and voltage drop reduction in the lower shell;

4) decrease of the anode to cathode distance;

5) prolongation of the aluminum pot lining life cycle.

The technical results will reduce the power consumption by 300-400 kWh and increase the current output by 1.5-2%, prolong the aluminum's pot lining life cycle by 6-8 months.

4. Conclusion

Titanium diboride is a more promising material to upgrade cathode blocks. It allows one to prolong cell's life cycle, reduce electric consumption of cell series due to reducing in voltage drop and driving down the anode to cathode distance. But the problem is the cost of the material which limits the usage of titanium diboride. This can be solved by low temperature synthesis using doped titanium dioxide, boric acid and a carbon reduction agent. The reaction mixture was heated by the 800-1000 °C in air atmosphere because of the possibility of forming other compounds. When the temperature rose to 800-1000 °C, a vacuum was installed in the system. Then heating to the soaking temperature of the system at 1050 °C with a vacuum 1-3 kPa was established for 3-4 hours. Modifying of titanium oxide with fluorine makes it possible in the $\text{TiO}_2\text{-C}$ system to carry out a complete phase-formation cycle in the $\text{Ti}_n\text{O}_{2n-1}$ series at temperatures below 1000 °C. Also successive phase formation of $\text{TiO}_2 \rightarrow \text{Ti}_n\text{O}_{2n-1} \rightarrow \text{TiBO}_3 \rightarrow \text{TiC}_x\text{O}_{1-x} \rightarrow \text{TiB}_2$ is realized in the $\text{TiO}_2\text{-B}_2\text{O}_3\text{-C}$ system under low-temperature synthesis conditions at 1030-1050 °C.

The obtained titanium diboride was grinded into a powder with a dominant fraction of 10 µm. This is 5-10 times smaller than the carbon graphite material used for the cathode blocks which were tested in a laboratory installation. In addition to the change in electrical conductivity that was higher on samples with titanium diboride, it was found that the modified blocks are wetted with aluminum. Anode to cathode distance can be reduced significantly due to aluminum wetting effects. The technical results will reduce the power consumption by 300-400 kWh and increase the current output by 1.5-2%, prolong the aluminum pot lining life cycle by 6-8 months.

Acknowledgement

The work is supported by state project № 13490SI/2018 of July 20, 2018 (The participant of the youth science innovation competition).

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