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# ANALYTICAL REVIEW OF THE FOREIGN PUBLICATIONS ABOUT THE METHODS OF RISE OF OPERATING PARAMETERS OF CATHODE BLOCKS DURING 1995–2014

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ABSTRACT

Increase of the part of graphitized cathode blocks used in the modern assemblies for production of primary aluminium via electrolytic method is recognized as the main direction of development of this technology. These blocks have a row of indisputable advantages, first of all low electric resistance and high level of electric conductivity. Increased abrasive hearth wear by alumina precipitants during melt motion seems to be the most important problem in operation of such blocks. This wear leads to decrease of service life of an electrolyzer and to increase of cost of manufactured metal.
The leading global producers conduct complex works directed on quality improvement of graphitized blocks. These works include a row of scientific directions: rational selection of raw materials, selection of optimal parameters of the technological process, different variants of impregnations etc. Most of researchers agree that rise of density leads to lowering of abrasive wear, and that this effect can be achieved via different ways (first of all by pitch impregnation). Several technical solutions (e.g. creation of variable electric resistance along block length, with lower value close to edges, in the areas with increased wear) have peen confirmed via production testing and are used now successfully at a row of metallurgical works.
In Russia graphitized blocks are not used practically. The project of Boguchansky aluminium works (planned to be put into operation in 2016) uses the blocks manufactured on the base of electrocalcinated anthracite with addition of 30 % graphite. Despite of the power engineering potential of Siberian region, such approach is inexpedient, taking into account the fact that high power expenses caused closure of a row of aluminium works in the European part of Russia. Accumulated global experience can be the base for development of science-intensive solutions in the Russian electrode industry and their consequent putting into operation, what in its turn will allow to achieve correspondence between quality of manufactured commercial products and requirements of customers.

## Introduction

Development of electrolytic method for production of primary aluminium due to increase of electrolyzer capacity leads to its substantial cost rising. In its turn, it defines more strict requirements to operating parameters of the materials used in the construction of aluminium electrolyzer [1].

It is known that the factors related to cathode lining make essential input (up to 50 %) in service life of an electrolyzer [2]. At present time graphitized cathode blocks are widely distributed, and their part in the new projects reaches 60v%. Lowering of specific consumмption of electric power for production of primary aluminium due to increase of conductivity of cathode lining is considered as the main advantage of usage of graphitized blocks [3]. It leads to decrease of cost of produced metal and, consequently, to rise of profitability of this industry [4].

The main problem of operation of graphitized cathode blocks is their increased abrasive wear that stipulates lowering of average service life of an aluminium electrolyzer [2]. Applying to the industrial conditions, large wear is observed in the areas with increased current density near block edges; in this case wear has typical W-formed shape. The features of abrasive wear for graphitized blocks is confirmed by multiple laboratorial investigations and examination of hearths of switched-off electrolyzers.

## Production technology

The conventional technology of production of graphitized blocks includes a row of consequent operations: classification of initial carbon material of filler; its mixing with pitch binding agent; forming; calcinating; pitch impregnation; graphitization with consequent machining.

We can emphasize several factors having the most effect on wear of final products. Density and porosity of a block depends on granulometric composition of initial carbon material; graphitization temperature determines electric resistance of a block and size of graphite crystallites; rise of electric resistance leads to increase of abrasive wear. It was supposed that vibroforming can contribute more isotropic structure to a block in comparison with extrusion [6], but input of this factor seems to be not essential, what is confirmed by the results of laboratorial investigations [7]. Improvement of operation characteristics of finished products can be achieved both by introduction of new stages in the production process and by optimization of the existing ones.

### Selection of the type of initial carbon material

The properties of initial carbon material are characterized by the tendency of correlation with the properties of finished products. Maximal level of structural ordering, typi-

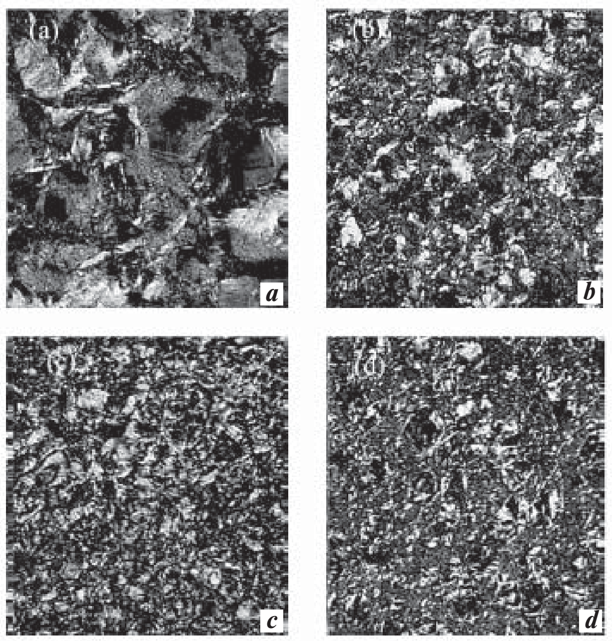

**Fig. 1. Microstructure of graphitized coke obtained from pitch with different content of $\alpha_1$-fraction:** *a* — 5%; *b* — 10%; *c* — 15%; *d* — 15% + 5% of hard coal [10]

cal for synthetic graphite, is determined by size and length of microparticles. Thereby quality of initial material can effect on such properties of cathode block as wearing resistance, thermal expanding, electric resistance and heat conductivity [2].

It is recognized in global practice at present time that pet coke is the initial material for production of the most qualitative graphitized blocks with high heat conductivity, low electric resistance and high stability to thermal shock. Relatively small amount of pitch in mixing is required for manufacture of blocks on the pet coke base. In this case the final product is characterized by high density and abrasive wear resistance.

Anisotropic microstructure of needle coke is the cause of relatively low parameters of such properties as mechanical strength, elasticity, coefficient of thermal expansion as well as higher rate of abrasive wear, despite high apparent density of final product [7]. Thereby, usage of isotropic pet coke (e.g. buckshot, manufactured from asphaltene-rich pet residues) is more preferred for production of graphitized blocks.

At present time anthracite is not used as the initial material for production of graphitized blocks. First of all it is caused by necessity of heat treatment at higher temperatures in comparison e.g. with oil coke (2800 °C and higher). In this case obtained graphite is characterized by less structural ordering than graphite manufactured in similar conditions but from other materials. Several sources [8, 9] describe investigation of the effect of anthracite additive in charge material on quality of finished products during manufacture production of graphitized cathode blocks in laboratorial conditions.

Cathode blocks produced via the method of manufacture of graphitized material [8] are characterized by electric conductivity that is suitable for operation at heavy-duty electrolyzers as well as by increased resistance to abrasive and sodium effect. Heat treatment is conducted at the temperature below 2600 °C and, respectively, graphitization of anthracite does not occur. Thereby the finished product actually presents material with the structure including graphitized matrix and non-graphitized particles of thermoanthracite.

The authors of the investigation [9] have conducted laboratorial researches and concluded that optimal values of electric resistance and tensile strength for compression of a block sample are achieved via mixing of anthracite and fine fraction of pet coke in relation 7:3. It should be noted that stability to abrasive wear was not determined in this research, but it can be supposed that it will be higher in comparison with blocks based exclusively on pet coke.

Usage of pitch coke is also one of the variants of production of high-dense graphitized cathode blocks. Presence of the fraction insoluble in benzazine-$\alpha_1$ in initial pitch is the key factor determining structure and properties of the finished electrode block on the base of pitch coke. This fraction provides termination of crystal growth in the process of pitch carbonizing (**fig. 1**). The same effect is achieved by adding hard coal to charge material [10].

The blocks have been produced on the base of coke obtained from pitch with different content of $\alpha_1$-fraction and consequently have been tested for wear. The level of abrasive wear for pitch coke with low $\alpha_1$ is close to that for blocks based on buckshot pet coke. Measured volume of abrasive wear decreased by 15% from the 1st sample to the 4th one, what corresponds to the hypothesis about correlation between this parameter and size of crystallites.

The source [11] presents the results of the most complete analysis of influence of raw materials on quality of graphitized blocks. Apparent and genuine density, electric resistance, heat conductivity, coefficient of thermal expansion, sodium expansion according to the Rappoport test and mechanical strength have been determined for the samples on the base of different materials. Fig. 2 displays the values of abrasive wear obtained via the method RDC-191 for samples on the base of different materials.

Acetylene black is characterized by low porosity what leads to decrease of pitch amount required for mixing (10%), allows to achieve lowering of abrasive wear value for hearth blocks (produced on the base of acetylene black) by 3–4 times in comparison with blocks on the base of buckshot pet coke. Low electric and heat conductivity are recognized as disadvantages of this material.

Shale coke should be emphasized separately: after heat treatment it has moderate graphitization [12]. Blocks on the base of shale coke allow to achieve acceptable level of mechanical parameters; at the same time they show the abrasive wear value comparable with the samples on the base of the best pitch coke grades and less by 2 times in comparison with the samples on the base of buckshot pet coke.

The authors of the investigation [8] have examined correlation between granulometric composition of the initial material and the properties of finished products. They have varied contents of fractions for the initial samples in such way: −8...+4, −4...+2, −2...+1, −1...+0,5 and −0,5 mm. The sam-

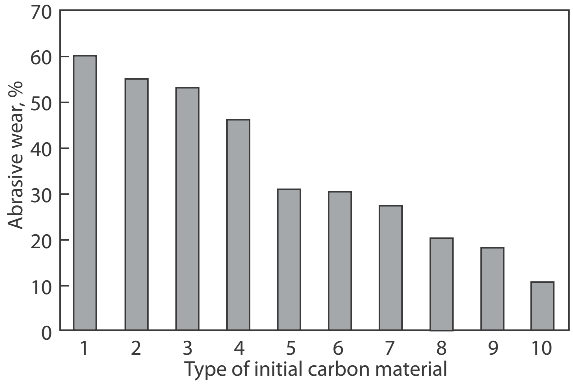


**Fig. 2. Influence of filler type on abrasive wear of graphitized cathode block (RDC-191) [11]:**
*1* — needle coke; *2* — anode coke with low S and V content; *3* — anode coke with average S and V content; *4* — low-sulphur coke; *5* — buckshot coke; *6* — coke from pitch with low content of $\alpha_1$-fraction; *7* — coke from pitch with high content of $\alpha_1$-fraction; *8* — coke from pitch with average temperature; *9* — shale coke; *10* — acetylene black

ple with the best combination of measured properties has balance of fractions 0:0:40:20:40 respectively. Increased content of fine fractions leads to decrease of electric resistance and substantial increase of density with favourable effect on mechanical properties (rise of bending resistance). This tendency is also noted in several patents for the method of production of graphitized blocks [13, 14].

### Variable resistance of cathode blocks

Graphitized blocks are characterized by W-form shape of wear (**fig. 3)** caused by gradient of current density. Patel et al. [15] have determined that rise of current density accompanies by intensification of electrochemical reaction of aluminium carbide forming. For lowering of this effect. It was suggested to use blocks with variable resistance along their length, when electric resistance of a block on its edges is higher than in the hearth middle.

It is possible to obtain variable resistance by different ways. It is known that electric resistance of a ready block is a function of processing temperature during graphitization and respectively all methods will be anyhow based on the local variations of the temperature procedure. According to the method described in [16], the block entering calcinating and graphitization has cross section larger in its edges than in its middle; excessive material will be removed later during machining. Achieving of the required effect is provided by difference of graphitization temperature along block length because electric resistance of a billet is inversely proportional to cross section square of each element. Additionally, variable resistance can be achieved by effect on graphitization process without varying billet size [17]. For example, it is possible to decrease thermal isolation of graphitized furnace in the areas corresponding to block edges or using special heat removing paths, as well as varying i electric resistance n the furnace for stamping that separates billets.

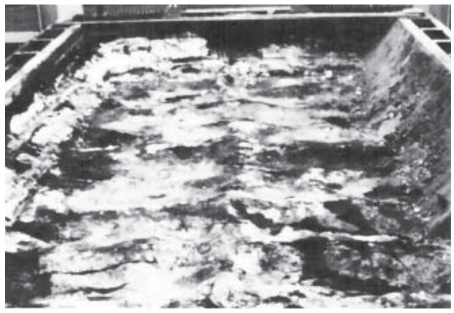

**Fig. 3. Hearth of electrolyzer with graphitized blocks having service live 1947 days [2]**

Several producers manufacture graphitized blocks of such type, and accumulated practical experience of their operation shows that variable resistance has no negative effect on technological process during aluminium production via electrolytic method [18, 19].

Impregnation of cathode blocks.

Impregnation of cathode blocks by pitch is one of the conventional methods for decrease of erosion wear in cathode block production. Pitch impregnated in open graphite pores lowers electric resistance of a block and its porosity after calcinating [7]. Coke forming in pores during calcinating is more hard and amorphous in comparison with graphite and at the same time less sensitive to forming of aluminium carbide. It is suggested that combination of these two factors allows to decrease total wear. The most complete impregnation can be achieved after combining preliminary vacuum treatment and consequent applying of excessive pressure [20].

The method of impregnation of cathode blocks by pitch for improvement of their operating parameters is realized after calcinating before graphitization [21]; it is similar to the method using in production of graphite electrodes for electric arc furnaces. Its realization causes variation of the properties of finished products: increase of density, decrease of porosity and electric resistance. The method of manufacture of graphitized products with adding up to 10 % of shale pitch in impregnation mix can be considered as an example [22].

Impregnation of blocks after graphitization is usually conducted at increased temperature, when pitch is in liquid state. Thereby content of the fraction that is non-soluble in benzazine (not more than 1%) is regulated, After impregnation, blocks are subjected to secondary calcinating at the temperature not more than 1600 °C. The following approaches can be applied in impregnation: usage of acid catalyst [23]; conduction of impregnation in vacuum conditions [24]; combination of excessive pressure of air and inert medium [25]. Other approaches also can be used but the general scheme remains unchangeable.

The researches connected with impregnation aimed on metal spraying of blocks are of great interest. The authors have investigated [26] influence of additives in charge materials required for manufacture of graphitized blocks containing 5–10% $ZrO_2$ or the same amount of comminuted alloy FeZrSi on the properties of finished products. Billets have been also impregnated by $ZrO_2$ suspension in phenol resin. After calcinating and graphitization at 2600 °C the obtained samples have displayed smaller erosion wear in comparison with reference data. It can be caused by forming of zirconium carbide with high hardness.

Similar tests have been conducted for impregnation by dispersed titanium dioxide. e.g. rutile or anatase. Surface of the samples after the tests was covered by crystallized cryolite and aluminium. Erosion rate was essentially lower in the areas where aluminium film was disseminated along the surface. The idea of titanium dioxide transformation in intermetallic compounds TiAl и $TiAl_3$ on the surface was suggested by the authors as the main concept of rise of wear resistance [26].

Impregnation of cathode blocks by solution, suspension or melt containing lithium compounds and their consequent calcinating can be also considered as a possible variant. Lithium compounds decrease substantially electric resistance of cathode blocks during electrolysis. If only part of cathode is impregnated, it is possible to achieve the effect of variation resistance with significant increase of average electric conductivity along cathode length; thereby usage of such blocks in high current electrolyzers is expedient. Such methods of impregnation for anthracite cathodes were described in the source [27], but the experiments including impregnation of graphitized cathodes have not been conducted at the present moment. The source [28] observes the scientific grounds of metal spraying on the surface of graphitized block due to lithium intercalation.

The authors [20] have analyzed the effect of quantity of pitch impregnation stages for samples on their abrasive wear. Experiments with static and rotating cathode have been conducted for joint evaluation of physical and chemical erosion mechanisms. In the second case, pitch impregnation increases substantially the rate of sample erosion in industrial scale up to 6–7 cm/g. Theoretically, rotation can increase the rate of electrochemical wear because it rises the rate of removal of forming aluminium carbide from cathode surface; it confirms limiting of electrochemical wear by the rate of aluminium carbide dissolution in electrolyte volume.

At present time, impregnated graphite and graphitized cathode blocks have been widely tested and used in commercial scale. It is recognized that impregnated graphitized cathode increases service life of electrolyzer approximately by 20%.

## Conclusions

Taking into account the development tendencies of electrolytic technology for manufacture of primary aluminium, it can be concluded that importance of solving the problem of improvement of operating parameters of graphitized cathode blocks will only increase. The complex approach including both optimization of initial raw material and introduction of additional stages in the technological process is recognized as the best method for its solving.

From the perspective of selection of initial raw material, it can be stated that turbo-stratified carbon materials are the most suitable. Small size of crystallites of synthetic graphite in finished blocks decreases essentially typical abrasive wear; additional charging of such materials as shale coke or acetylene black can also additionally facilitate this process. Scientifically substantiated collection of combinations of different kinds of raw material allows to improve quality of graphitized blocks; however, this theme has not been researched yet.

Different variants of pitch impregnation and creation of variable resistance along block length should be emphasized among the methods directed on improvement of operating parameters after their testing in the industrial conditions. Both of these approaches can rise substantially service life of blocks, however, impregnated blocks are more susceptible to wear than cathodes manufactured via variable resistance technology. Obtaining of the hearth softened by molten aluminium during its metal spraying owing to forming of aluminium-based intermetallics has large practical importance. This concept seems to be the most interesting for further examination and development.

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