THE ELECTRICAL CONDUCTIVITY OF THE HIGH CONTACTS BETWEEN NATURAL CRYSTALLINE GRAPHITE FLAKES

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Introduction.

Clamping electric contacts are characterized by section of spots of contacts and a condition of surfaces contacting bodies. At definition of conductivity of powders of measurement spend in standard conditions. At use of powders of flake graphite compression in a measuring cell causes their grain orientation. Lines of a current pass through particles, electrically connected in places of mechanical contacts. In places of contacts transitive contact resistance as additional to ohmic electric resistance is formed. Formation of transitive resistance it is caused tightening of lines of a current to clamping spots of contacts, and also electric resistance of a surface of contacts. Clamping contacts are characteristic for compositions of high filling when binder is dielectric. In lamellar polycrystals of graphite between anisotropic on conductivity crystal grains there is a contact electric resistance. It is formed at tightening lines of a current to spots of contact between agglomerate crystalline grains. In particular, agglomerate contacts are formed between particles at baking binder at use carbon of ceramic technology. At baking binder there is a transition from clamping to agglomerate contacts. Effect of increase in area of spots of contacts there are difficultly enough interpreted as depends on the form of spots of contact, conditions of a surface and features of passage of an electric current in grains of filling powder. For the control of these parameters modeling samples on the basis of flake natural graphite have been specially made. The electric current flows through grains by means of mechanical contacts. After baking electrically transparent coke of binder layers increases area of spots of contact.

In work [1] results of research of change of electrophysical properties of a composition natural graphite - binding are resulted at temperature interval of backing and graphitization. Diameter of samples was 8 mm. The used powder of natural graphite contained an insignificant impurity of the dissolved borum. It has been established, that backing increases conductivity by two orders from $\sim 10^3$ up to $\sim 10^5$ Siemens, transverse magnetoresistance on the order from 3 up to 30 %, also reduces value of a Hall constant in some times. This results are repeated with use natural flakes specially cleared of an impurity of borum [2]. Change of contact resistance investigated with use of electrophysical methods. The additional information have received from relative, not dependent on porosity of a material properties - anisotropy of conductivity and magnetoresistance. Last are measured at three perpendicular directions of the sample in a magnetic field, at 300 and 80K.

Experiment

Laboratory samples on the basis of natural flake graphite from Taiginka deposit have made by carbon ceramic technology. As filler have taken a unimodal powder of fraction-0,16 + 0,05 mm. Coal pitch (30 %) was a binder. At mixing the coal pitch extends on a surface of a flakes. Pressing was made a method of extrusion through calibre in diameter of 35 mm. Preparations thermally processed for baking and graphitation a bind pitch. Heat treatment of samples was made in steps in an interval 400 - 1200^{0}C, with endurance at the maximal temperature 0,5 hours. A microstructure investigated methods of optic microscopy. Microsections was made of green samples, in a plane both lengthways, and it is perpendicular to a direction of extrusion.

According to optical microscopy unimodal flakes at mixing keep within packages. At extrusion mass through caliber the arrangement of packages is condensed due to plastic deformation of flake edges. At moving layers of mass packages are guided and extended along a direction of extrusion. Thus the sequence of packages forms pouring structure in the central part of samples. In a perpendicular direction orientation of packages are chaotic. Squeezing at pressing deforms flakes inside of packages and redistributes a pitch with formation fan-shaped arrangements of flakes in packages. Crumpled in the field of contacts flakes form the mechanical skeleton kept at hardening of cooled samples.

Results and Discussion

Electrophysical researches carried out with measurement of electrical conductivity, magnetoresistance and Hall constant. Samples cut out from the central part of samples, up and down to a direction of extrusion. Measurements spent at three perpendicular positions of the sample in a magnetic field, at 300 and 80K, put the holder to liquid nitrogen. Determined value of $\Delta\rho/\rho$ summarizing results of measurements at three perpendicular orientations of sample in magnetic field. This lets to lead complex analysis of electrophysical properties for characteristic of feature of dissipation of energy, estimation of size of blocks of mosaic and texture of carbon materials.

Electronic properties of a basic layer of graphite are described with use two zone models with approximately equal concentration n and mobility μ_a electrons and holes. Value of conductivity σ_a and magnetoresistivity $\Delta\rho_a/\rho_a$ at intensity of a magnetic field H determine with use of formulas:

$$\sigma_a = (en\mu_a); \qquad \Delta\rho_a / \rho_a = \mu_a^2 H^2 \qquad (1)$$

From (1) follows, what mobility ratios, calculated on values of conductivity and magnetoresistance at 300 and 80 they are in the ratio:

$$(\mu_a)_{80} / (\mu_a)_{300} = [(\Delta\rho_{a`} / \rho_a)_{80} / (\Delta\rho_{a`} / \rho_a)_{300}]^{0,5} = (n_{300} / n_{80})[(\sigma_a)_{80} / (\sigma_a)_{300}]. \qquad (2)$$

Conformity to expression (2) is used for the characteristic of conformity of electronic properties of artificial graphites to graphite monocrystal.

For the analysis of character energy dissipation at flakes contact in a composition used modelling non-uniform course of an electric current on annealed pyrographite plates. The modelling sample cut out from annealed pyrographite in the form of a plate with the sizes 2 x 9 x 33 mm. Modelling of variable conditions of electric connection created change of depth of cuts between covered with cuprum end faces of the lamellar sample. Two cuts settled down near to end faces, the third in the middle on the opposite side. Depth of cuts consistently increased through 0,2 mm. This provided increase of part of energy dissipation from passing of electric current across layers of graphite. Parities relative size for σ and cross-section magnetoresistance $\Delta\rho / \rho$ are resulted on fig. 1. For comparison relation for polycrystalline graphite of industrial electrodes are shown.

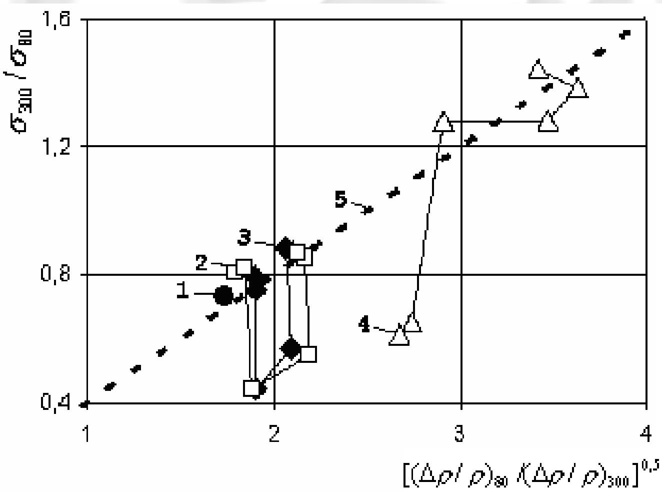

Fig. 1. Interrelation between $(\Delta\rho / \rho)_{80} / (\Delta\rho / \rho)_{300}$ and $\sigma_{300} / \sigma_{80}$ for various graphite. 1 – industrial electrode; 2, 3 – flake graphite composition with various temperatures of baking, up and down textures accordingly; 4 - the modelling sample from annealed pyrographite with cuts of various depth; 5 - settlement according to for a basic layer. Lines between points correspond to increase of temperature of baking of samples of composition on basis of natural graphite, and also increase of depth of cuts on modelling pyrographite sample.

From fig. 1 it can see, that discrepancy of experimental values expression (2) is observed at samples of composition in the field transition from clamping contacts to agglomerated.

At baking an investigated composition on the basis of natural flake graphite such relative properties, as anisotropy of conductivity and anisotropy of magnetoresistance components at three perpendicular positions of the sample in a magnetic field do not change.

Performance of a expression (2) characterizes absence of the significant contribution from passing of electric current across layers of graphite and from change of a way of connection flakes in a composition. So the structure near-surface layers of graphite flakes corresponds to structure of electrode graphite. If the size of blocks of a mosaic makes 2 mkm in monocrystall natural graphite, in electrode graphite the size of blocks of a mosaic reaches ~0,5 mkm. Evaluation demonstrate, that thickness of a near-surface layer is modulated by the linear sizes of a spot of contact. So, for flakes with 100 mkm in diameter average thickness makes hundreds of nm, and a primary power failure on contacts to the minimal thickness in view of increase in resistance defects of structure in tens of nm. On samples on the basis of the cleared graphite with various temperatures of heat treatment a constant of the Hall measured separately at 300 and 80K. It is established, that at the baking of samples the size of a Hall constant is not great and passes through zero value. It is possible to believe, that deficiency leads to increase of concentration of holes. It is appreciable on the samples made of natural graphite with an impurity of borum. For electrode graphite an expression (2) are carried out (fig.1). That corresponds a composition on the basis of natural graphite with agglomerated and also clamping electric contacts.

Thus, current lines for clamping contacts repeat that's in agglomerated contacts, but with smaller contacts area. Baking reduces specific resistance of binder and through decrease defective near-surface layers influence. Perhaps, that formation of a near-surface layer with raised defectiveness on a surface of flakes is induced by mechanical damages at dressing of natural graphite, and also compression and deformations at moving of mixed mass during pressing samples by extrusion.

Reference

[1] Dmitriev A.V. Scientific Fundamentals of the Development of Procedures for Decreasing the Specific Resistance of Graphitized Electrodes (rus), Chelyabinsk: ChGPU, 2005.

[2] Dmitriev A.V. Investigation of contact electrical resistivity of graphite crystals in polycrystal. The final report. Grant RFBR 04-02-96057-p2004ural_a, 2005.

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