SYNTHESIS OF β-SiC IN THE INTERMEDIATE LAYER OF CORUNDUM COATINGS BASED ON A SOL-GEL BINDER FOR PROTECTING GRAPHITE OBJECTS FROM OXIDATION

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A coating is developed for protecting graphite from oxidation at 2023 – 2223 K. The efficiency of the protective action of a corundum coating based on a sol-gel binder increases due to creating a dense intermediate layer between the graphite substrate and the coating as a result of its self-reinforcement with fibers of mullite crystals and β-SiC nanoparticles. Components of a modifier and sol-gel binder, but not carbon of the graphite substrate, provide synthesis of β-SiC.

Keywords: graphite oxidation protection, corundum coatings, silicon carbide, mullite, self-reinforcement, dense intermediate layer.

Reliable use of graphite at high temperature is possible in an inert gas atmosphere or in a vacuum. Objects made of graphite and refractory graphite-containing materials often serve at elevated temperature in an oxidizing atmosphere. Under normal conditions graphite is very inert, but above 673 K it oxidizes with oxygen from air to CO, and above 773 K to CO_2. Operation in an oxidizing atmosphere is accompanied by a reduction in material strength. There is an increase in pore volume and growth of permeability. With an increase in temperature there is an increase in oxidation rate as a result of an increase in graphite material porosity. The CO and CO_2 gases formed are removed from the surface of an article, promoting further graphite oxidation and burning of it. Burning rate depends to a considerable extent on temperature and the rate of oxygen influx.

If the surface of a graphite component is not protected from oxidation during firing, then at about 1573 K the graphite burns by 10 – 15 mm [1]. A reduction in graphite strength during its oxidation is connected with development of porosity [2], and development of porosity leads to a reduction in strength. Failure of graphite proceeds through the coke of a binder, which reacts with oxygen. Bridges, which form the coke binder between filler grains are oxidized, burn away,

and this leads to marked loss of strength with a significant material weight loss [3].

Due to a collection of valuable physicochemical properties graphite is used in many branches of industry. The high heat resistance gives rise to use of graphite in many domestic refractory objects, including those used in rocket construction, and as a result of chemical graphite is used in chemical engineering as a structural material; the low friction coefficient of graphite makes it possible to employ it for antifriction components, and high electrical conductivity makes it possible to use it as an electrical engineering material and components, heaters, electrodes, etc. It is well known that graphite is used in nuclear technology and other areas.

Graphite is used in rocket building for manufacturing linings for rocket nozzles, operating on solid fuel, nose cones and other components. The nozzle for a solid fuel rocket should operate in an oxidizing atmosphere for 35 sec in all. It is necessary to guarantee travel of a rocket into a near-earth orbit, providing a ten- to fifteen-fold life of nozzle material. Artificial graphite machines well, although the field of its application is limited by a tendency towards oxidation and erosion at high temperature. Therefore the question of protecting carbon materials is urgent and its solution is an important task.

Several methods exist for protecting carbon materials from oxidation. Particular attention is devoted to protective

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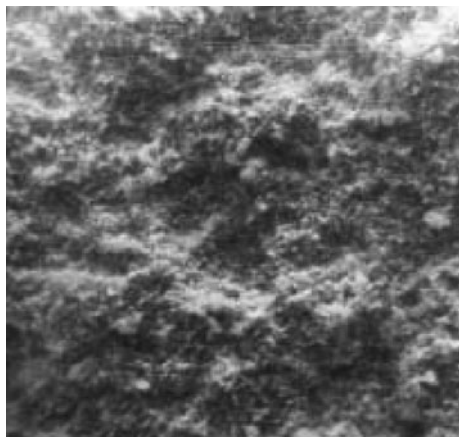[2] Institute of Chemistry of the KomiNTs, Uro RAN, Syktyvkar, Russia.

Fig. 1. Fracture surface of self-hardening coating based on corundum 10 h after application to a graphite component. ×3500.

coatings for graphite components. Creation of protective coatings is closely connected with questions of reaction at the phase interface, when there is diffusion of carbon into a refractory compound, and consequently rebuilding of its lattice, but not for graphite. Therefore, within the volume of graphite, close to a contact boundary there is formation of significant porosity [4], which intensifies graphite material oxidation. In contemporary technology considerable important is attached to creating protective coatings providing a saving of expensive materials.

Available coatings for graphite have insufficient gas tightness, which does not provide prolonged operation of graphite structures above 1473 K. The requirement for reliable protection of graphite materials from oxidation requires improvement and creation of new coating compositions and a study of their protective function towards oxidation.

The aim of this research was to develop a self-hardening corundum coating for graphite components, a capacity to increase their life in an oxidizing atmosphere by creating an intermediate barrier layer with synthesis of newly formed β-SiC from components of silicon alkoxide and mullite in the matrix of a corundum filler from the latter and ultrafine SiO_2 sol-gel binder.

It is well known that an increase in thermal shock resistance of corundum material is achieved by introducing additions into a mix promoting mullite synthesis, and also ZrO_2 and SiC [5]. Formation of mullite at low temperature may promote an increase in strength of an adhesive coating.
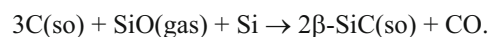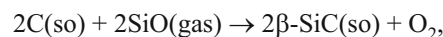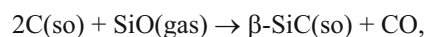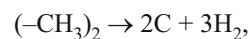
In creating coatings the filler used was oxides of Al_2O_3 and ZrO_2, and the binder used was self-hardening sol of oxide salts and organosilicon, obtained by acid (HNO_3, H_3BO_3, H_2SO_4, HCl) hydrolysis of a substance with a different quantity of water, including different modifying addition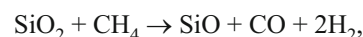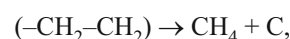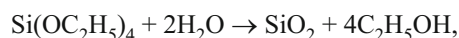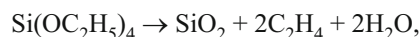s, which have a favorable effect on the synthesis of β-SiC in the intermediate layer and on protection from corrosion. In order to increase graphite material coating density and adhesion to the graphite substrate, reduce shrinkage and oxidation capac-

ity the organosilicon binders used were of sol-gel composition [6 – 9], and fillers were modified with silicon alkoxide.

The sol-gel process makes it possible to accomplish diffusion of active amorphous oxide of the binder at normal temperature in microdefects of a graphite body to a depth of 10 – 40 μm, which increase coating adhesive strength to the graphite substrate (Fig. 1).

Coating strength in a raw condition is a result of polymerization of organosilicon binders with formation of ≡Si–Î–Si≡ bonds; the increased density and strength after firing is a result of intensification of sintering of corundum mixes with introduction of ultrafine SiO_2. During heat treatment there is sol decomposition with formation at 773 K of particles of atomic carbon and ultrafine silica, which remains in an amorphous condition at above 1273 K, and this accelerates sintering. It is established that the fineness of silica particles and its transformation into one of the crystalline forms at 1273 – 1373 K depends on sol preparation conditions.

Creation of specific conditions of the surrounding atmosphere promotes synthesis of β-SiC nanoparticles from atomic carbon and silicon monoxide [10]. The mechanism of low-temperature β-SiC synthesis from silicon alkoxide, which is component of the modifying additions and sol-gel composition, during mechanical activation and self-organization of components of the system $Si–O_2–C$ includes the following:

$$Si(OC_2H_5)_4 \rightarrow SiO_2 + 2C_2H_4 + 2H_2O,$$

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH,$$

$$C_2H_5OH \rightarrow CH_4 + H_2 + CO,$$

$$(-CH_2-CH_2) \rightarrow CH_4 + C,$$

$$SiO_2 + CH_4 \rightarrow SiO + CO + 2H_2,$$

$$SiO + H_2 \rightarrow Si + H_2O,$$

$$(-CH_3)_2 \rightarrow 2C + 3H_2,$$

$$2C(so) + SiO(gas) \rightarrow \beta\text{-SiC(so)} + CO,$$

$$2C(so) + 2SiO(gas) \rightarrow 2\beta\text{-SiC(so)} + O_2,$$

$$3C(so) + SiO(gas) + Si \rightarrow 2\beta\text{-SiC(so)} + CO.$$
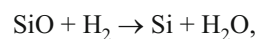
Due to use of the sol-gel technology elements in creating coatings a dense intermediate layer was formed [9] of corundum reinforced with β-SiC nanoparticles and filaments of mullite crystals, creating an impenetrable barrier for carbon diffusion from a graphite object with this coating into filler oxide even at high operating temperature (>2000 K).

Uniformity of sol-gel ultrafine particle distribution over the surface of a refractory filler determines the intensity of

SiO_2 particle reaction with it in relation to the thermodynamic potential of reaction with filler, improves coating properties by sintering or formation of new phases (Fig. 2), which improve the coating operating properties. A coating heat treatment regime has been developed providing formation of a dense thermal shock resistant structure and a prescribed phase composition.

It is interesting to study the protective properties of coatings in self-hardening binders and to study the intensity of graphite material oxidation at high temperature after forming a protective coating during firing by the regimes developed [11].

As is well known, coating thickness is one of the important characteristics governing its protective properties and endurance of graphite materials. An increase in coating thickness does not always improve protective properties and quality, since such indices of these properties, as adhesion, bending resistance, and some others, are worsened. In our case the coating layer thickness on the basis of self-hardening corundum mix based on organosilicon binders did not exceed 600 μm. Coatings were applied to the surface of graphite specimens of different grades. Adhesion of coatings based on sol-gel binders at the surface of silicided graphite is better than for coatings based on other binders. The protective properties of coatings was tested after their formation on silicided specimens. The tests were performed in a hot compaction press in an atmosphere of freely circulating air.

The main layer with a thickness of 0.5 – 0.7 mm has a dense structure, and it consists mainly of corundum and mullite. Mullite covers grains of corundum with a network of needles. At the surface between corundum grains within the body of a coating there is also formation of fine mullite grains with a size of 1 – 2 mm (Fig. 3). Contact of a coating with graphite after testing is so strong that coatings during testing fro adhesive strength are removed together with graphite platelets. Coatings penetrate deeply into structural defects of a graphite specimen.

A diffusion coating of lusterless color covers graphite flakes of the substrate and is present in pores (Fig. 4). Fine crystals of new formations are seen in coatings. A sol-gel composite diffuses into microcracks and other microdefects of a graphite specimen, which increases coating adhesive strength with the graphite immediately after application and especially after heat treatment as a result of forming SiC and mullite phases, increasing coating heat and thermal shock resistance.

Formation of SiC and mullite from binder components with reaction of SiO_2 of the binder with corundum filler of the coating promotes compaction of the intermediate layer [9]. Formation of mullite in the form of needles both in areas of graphite specimen defects, and in the intermediate layer and body of a coating promotes an increase in coating adhesive strength with a graphite substrate, reducing coating LTEC and providing an increase in its thermal shock resistance.
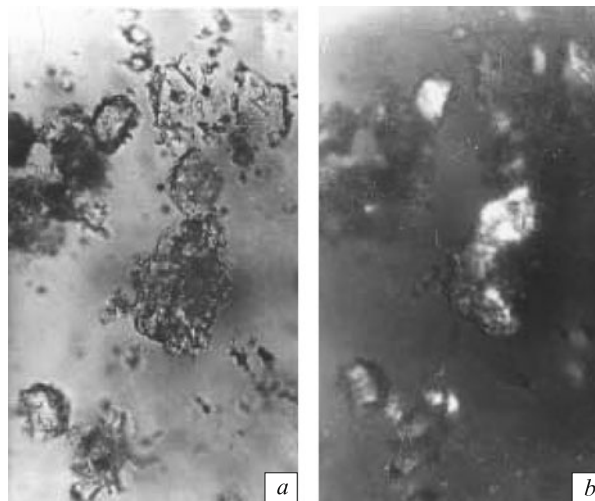

Fig. 2. Grain of corundum coating filler with a network of mullite needles at the surface: *a*) without analyzer; *b*) with crossed nicols. ×280.

Fig. 3. Coating diffusion within a graphite component during heat treatment. ×1600.
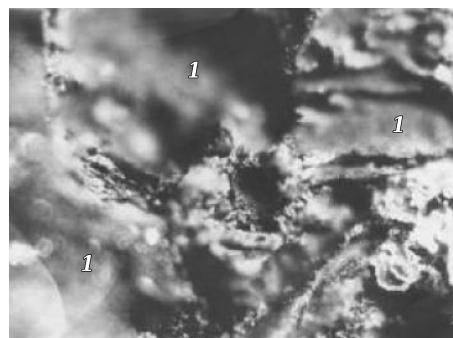

Fig. 4. Detail of the graphite substrate structure after heat treatment, i.e., graphite flakes, covered with coating diffused into the graphite body: *1*) lusterless substance of a coating material based on flaky graphite within a graphite body. ×750.

Results of tests showed that the best resistance to oxidation is exhibited by coating S-3 [11], which sinters well at 1673 K, does not have a glassy form, and retains high adhesion to the silicided graphite after testing at high temperature.
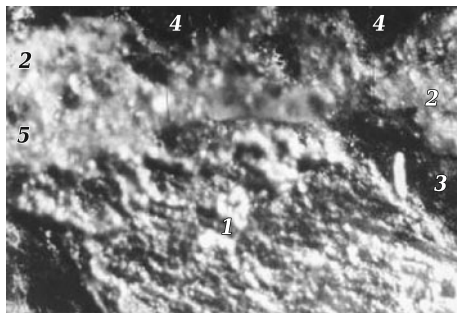
Fig. 5. Area of future breakthrough of a coating over pores between a graphite substrate and a coating after testing at 1973 K (exposure 15 min, transverse section of coating contact with graphite substrate): *1*) graphite component; *2*) coating; *3*) pores in coating-graphite boundary; *4*) area of noticeable breakthrough; *5*) intermediate layer. ×2400.

On firing there is formation of an intermediate layer (Fig. 5) which is strong and reliably retains the coating at the surface of silicided graphite, prevents carbon diffusion from the graphite substrate into the main layer, and thereby retards development of diffusion oxidation of graphite and provides short-term resistance to oxidation of silicided graphite even at 2023 – 2063 K. Up to 2023 K the coating does not fail or have points of breakthrough. Points of noticeable breakthrough develop above 2023 K. In prolonged testing a coating of S-3 is retained at the surface of a whole specimen at 1973 K.

Results of petrographic study of a coating and its contact with a graphite surface after testing at 1973 K showed the following. Diffusion of coating into the graphite substrate is observed to a depth of 300 μm through microdefects. In the contact there are pores filled with fuzed substance. At the boundary between graphite and the coating a dense intermediate layer is seen with a thickness of several microns. The prescribed phase composition of this layer forms during coating firing. The main layer of a coating during service is mullitized. The surface of corundum grains and binder mix is penetrated by a network of mullite needles with a size of 1 – 2 μm, which strengthens the material and increases resistance to temperature drops. The degree of burning of carbon of graphite objects, protected with a thin layer of coating, consists of a corundum sol-gel composition, at 1973 K (exposure for 15 min) it was less than 1%, and there is no oxidized zone.

As indicated above, coating S-3 has a high resistance to oxidation up to 2023 K. Since temperature control during testing was carried out from the side surface temperature of graphite specimens, coated with a layer of the composition developed, then the temperature recorded was reduced at a minimum by 100 – 200 K, as a result of which the coating exhibits significantly less luminosity during heating, than silicided graphite, i.e., the actual possible operating temperature is 2123 – 2223 K.

Thus, theoretical prerequisites have been fro synthesis of β-SiC at low temperature in mechanically activated electrocorundum by silicon alkoxide both in an air atmosphere and in an argon atmosphere. The coating composition and technology developed for its preparation made it possible to provide high oxidation resistance of silicided graphite at up to 2023 K.

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