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PROTECTION OF GRAPHITE AND GRAPHITE-CONTAINING MATERIALS FROM OXIDATION

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The results of a comprehensive study of newly synthesized single-layer and multiple-layer coatings based on modified corundum for protection of graphite from oxidation are reported.

Graphite is chemically inert at high temperatures and does not enter into a reaction with acids, alkalis, and with basic and acid slags; it undergoes no deformation, and its strength tends to increase somewhat with temperature. Graphite displays an exceptionally high thermal stability; its elastic modulus is two orders of magnitude smaller than that of sintered ceramics. The structural features of graphite are reflected in its unique properties, in particular, electric conduction, which permits its use for fabricating electrodes. Graphite, owing to its structural zonality and granular composition, is an attractive material for use in the production of corundum-graphite, magnesia-carbon and other refractory components [1].

An intriguing property of graphite is that it improves its strength with temperature; this behavior may be explained by the enhancement of intercrystalline bonding on heating and by the reorientation of grains in a loading direction, also by the reduced internal stress generated because of the reduction of the anisotropy of thermal expansion of the crystalline graphite. Another benefit of graphite is that it can be used as an antifriction material capable of operating without a lubricant. Under the service conditions of an electric vacuum furnace, it is only lubricants with a high vaporization temperature and low vapor pressure that are capable long-term performance. Antifriction properties of graphite come from its layered structure: under shear forces applied, the graphite layers undergo mutual displacements since the interlayer bonding in graphite is much weaker than the interatomic bonding within the layer.

Graphite materials at high temperatures can effectively be used only on condition that no chemical reaction occurs between the graphite-mating parts (coatings among them).

Another important concern is the eventual interaction between graphite and the burning furnace environment, or during the service of graphite components. Reliable high-temperature service of graphite is possible in an inert atmosphere or under vacuum. In the high-temperature technology, artificial graphite is typically used that is prepared by a thermal graphitization method [2, 3].

Components made of graphite and refractory graphite-containing materials are frequently intended for service at elevated temperatures in an oxidizing medium. Under normal conditions, graphite behaves as an inert material. Graphite is oxidized by the atmospheric oxygen to CO at temperatures above 673 K, and to CO₂ — at above 773 K. Graphite, when operating in an oxidizing medium, loses some strength, concomitant with an increase in pore volume and permeability. The increase in porosity accelerates the oxidation of graphite material with temperature. The gases CO and CO₂ as they are removed from the surface of a component, promote the oxidation and burnout of graphite. The burnout rate is mainly controlled by the temperature and flow rate of oxygen.

The more perfect the crystal structure of graphite, the higher the oxidation onset temperature. The oxidation is accelerated in the presence of Fe, V, Na, Cu and some other metals; by contrast, Cl₂, phosphorus and boron compounds produce an inhibitory effect. Halogen atoms are capable of incorporating into the crystal lattice of graphite to form inclusion compounds that are stable in neutral media or under vacuum when heated to 1473 – 1773 K. Graphite is virtually inert towards the nitrogen molecules, and graphite components can operate in a nitrogen atmosphere at temperatures up to 2773 K. Graphite enters into a reaction with gaseous hydrogen at 573 – 1273 K to form methane.

In a graphite component whose surface is not protected from oxidation, the graphite materials burns out to a depth of

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10 – 15 mm at a temperature of about 1573 K [4]. Oxidation of graphite involves a decrease in strength and increase in porosity [5]; of the two processes, the former develops at a higher rate. Degradation of graphite proceeds by a mechanism involving oxidation of the coke (a product of the binder). The coke bridges linking the filler grains undergo oxidation (in fact, burn out), which results in a significant loss of strength; the loss of mass of the material is insignificant [3].

Graphite, owing to its valuable physicochemical properties, has found application in many sectors of industry. The high-temperature strength makes graphite the most suitable refractory material for many heavy-duty engineering components, in particular, in rocket engineering; graphite, owing to its chemical stability, is used as structural material in the chemical engineering industry; the low friction coefficient makes it possible to use graphite as antifriction material for tribo-couples; owing to its high conductivity, graphite is used for fabrication of electric engineering materials and components, heaters, electrodes, etc. Uses of graphite in the nuclear technology and related fields have also been reported. In rocket engineering, graphite is used to fabricate the nozzle inserts for solid-propellant missiles, nose cones, and other rocket parts. In a solid-propellant rocket, the nozzle should operate during a period of 35 sec in an oxidizing medium. The guaranteed settling of a rocket into orbit can be effected only using a material for the nozzle with a 10 – 15-fold nominal stability margin. Artificial graphite is a well-processable material, but the area of its application is somewhat limited because of the oxidation and erosion at high temperatures; therefore protection of carbon-based materials has been and continues to be a challenging problem.

Several methods for protection of carbon materials from oxidation have been proposed. A frequent technique for protection of graphite materials is to impregnate them with molten high-melting metals and their alloys. Graphite-carbide composites are thus obtained that display an enhanced temperature resistance to oxidation, a high strength and high corrosion stability. Another technique involves preparation of multi-component materials based on powdered high-melting compounds and graphite by hot pressing or sintering. Graphite as a constituent of the composite provides high thermal stability and good machinability of the material, and high-melting constituents impart special properties to it. However, these methods are energy-consumptive and impracticable for protecting large-size graphite components from oxidation.

Protective coatings for graphite components have been an issue of special concern. Development of protective coatings is closely related to interactions at the phase boundary where carbon diffuses into high-melting materials, which causes a rearrangement of their (rather than of graphite) lattice. Therefore in the bulk graphite, near the contact boundary, a significant porosity is produced [6], which promotes the oxidation of the graphite material. In each particular case, issues of major concern are the coating technique used and

the availability of facilities that would enable the pre-service heat treatment of coated graphite components considering that the adherence of coating to the graphite surface and continuity of coating control mainly the resistance of graphite component to oxidation.

Multilayer coatings for protection from oxidation have been developed [7]. These coatings could significantly extend the service life of graphite under high-temperature oxidation conditions. To further improve the resistance of graphite to oxidation, the multilayer coatings were heat-treated in an inert medium. It should be kept in mind, however, that seemingly insignificant flaws in the coating may result in a catastrophic oxidation.

In modern technologies, much attention has been focused on the development of protective coatings capable of economizing on expensive materials. According to [8], the limiting temperatures that permit safe contact of various oxides with carbon are: Al_2O_3 , 1923 K; BeO, 2253 K; MgO, 1923 K; SiO_2 , 1753 K; ZrO_2 , 2253 K; $\text{MgO} \cdot \text{Al}_2\text{O}_3$, 1523 K, etc. Of interest are also combinations of carbon with BaO, Cr_2O_3 , and carbides and nitrides of silicon. It is generally believed that in carbon materials interacting with high-melting oxides, the diffusion processes at the phase boundary are mostly unidirectional in character, that is, the diffusate is predominantly carbon. The oxides interact with carbon to yield gaseous products, which finally results in the buildup of a SiC layer at the contact boundary. The dense carbide layer thus formed behaves as a barrier to inhibit the diffusion of carbon. Zirconium, silicon, titanium, and chromium dioxides have been used to make coatings [6, 9]. Above 1830 K, graphite undergoes oxidation on interaction with oxides, primarily with SiO_2 . The aluminosilicate bond fails to provide full protection to graphite from oxidation because of the increased porosity coming from the interaction between carbon and SiO_2 . Introducing crystalline silicon to the mixture improves significantly the physicomechanical properties and resistance to oxidation of graphite-containing refractories [10]. In a reducing medium, β -SiC is formed by the reaction $\text{Si} + \text{C} \rightarrow \beta\text{-SiC}$. The unreacted silicon under oxidizing conditions converts to cristobalite which, when melted, closes pores in the graphite-containing material and thereby restricts the access of oxygen to carbon. In certain cases, the glazing technique can be used to protect graphite from oxidation. To inhibit the oxidation of graphite components, these were subjected to multiple impregnation process under vacuum using a mixture of aluminum salt solutions and aluminum oxide sol followed by heat treatment. Tetraethoxysilane and ethyl silicate sols were used to that purpose in treating corundum-graphite refractories. In graphite-containing components heat-treated at 1273 K, β -SiC was observed to form from gel constituents [10 – 14].

Carbides that are synthesized during the burning process are likewise susceptible to oxidation. The oxidation of carbides was carried out at temperatures: SiC, 1473 – 1873 K; ZrC, 1773 K; B_4C , 1373 K, and MoC, 1173 K. It was shown

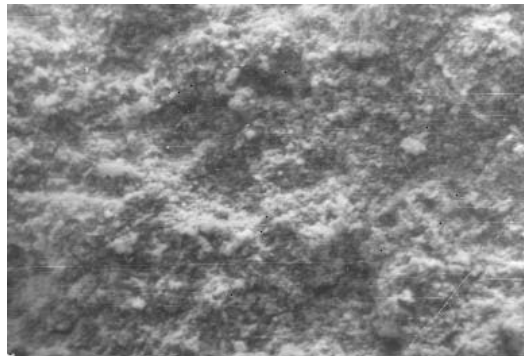


Fig. 1. Fracture surface of a corundum-based self-hardening coating (photomicrograph taken on day 10 after application to the graphite substrate; $\times 3500$).

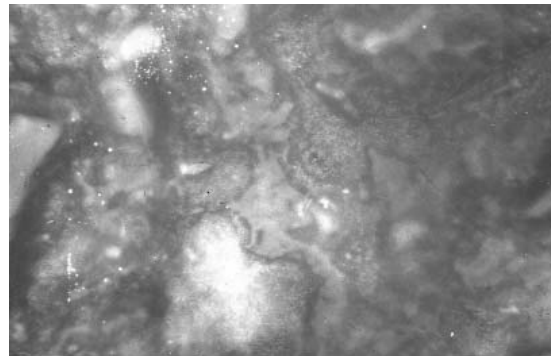


Fig. 2. Photomicrograph of the newly-formed material between corundum grains and on the surface thereof (heat-treated at 1272 K; $\times 1000$).

in [4] that the long-term service life of an oxide coating at a particular temperature is controlled by the mechanism of oxide reduction and by properties of the carbide layer formed. The dense carbide layer formed in the contact zone performs as a barrier to the diffusion of carbon into the oxide coating, and for this reason the maximum exposure temperature may even be higher than the temperature for the onset of interaction between oxide and carbon. Just such behavior was observed for carbon interacting with zirconium, silicon, titanium, and chromium dioxides. With carbides of aluminum and magnesium, no continuous carbide film was observed to form at the oxide – boundary. Plasma-assisted coatings based on Al_2O_3 and glass-like bond provided safe protection for graphite from atmospheric air only below 1773 K, at 2073 K, the protection was of rather short duration.

The air tightness of available coatings for graphite is seldom sufficiently high, which renders graphite components unsuitable for long-term operation at above 1473 K. Further efforts are required from research and industry to develop new coatings capable of protecting graphite components from oxidation.

Our goal in this study was to develop a self-hardening coating that would enhance the stability of graphite compo-

nents in an oxidizing medium by creating an intermediate barrier layer.

It has been established that the enhanced thermal stability of corundum materials could be attained by introducing additives to the mixture that are capable of promoting the synthesis of mullite as well as of ZrO_2 and SiC [15]. The low-temperature mullitization can also enhance the adhesive strength of refractory putty. Since Al_2O_3 and ZrO_2 , rather than BeO , judging from the limiting temperature of safe contact with carbon, are more suitable and cost-justified for the purpose, they were selected for use as fillers; the binder were self-hardening sols of hydroxy salts and organo-silicon compounds obtained by acid hydrolysis (HNO_3 , H_3BO_3 , H_2SO_4 , or HCl). Various modified additives promoting protection from the oxidation were also used.

Sol-gel compositions have also been used as organo-silicon bonds to increase the density of coating and adhesion to the graphite substrate and to reduce shrinkage and oxidability [16 – 19].

The sol-gel process allows diffusion of the active amorphous oxide of the bond into the graphite bulk (through microscopic structural imperfections) to a depth of 10 – 40 μm , which enhances the adhesive strength of the coating to the

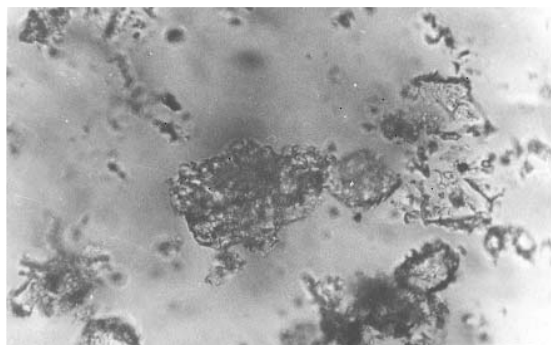


Fig. 3. Photomicrograph of a grain of the coating filler (a network of mullite needles is visible; $\times 280$).



Fig. 4. Photomicrograph of a coating material diffused into the graphite bulk (heat-treated; $\times 1600$).

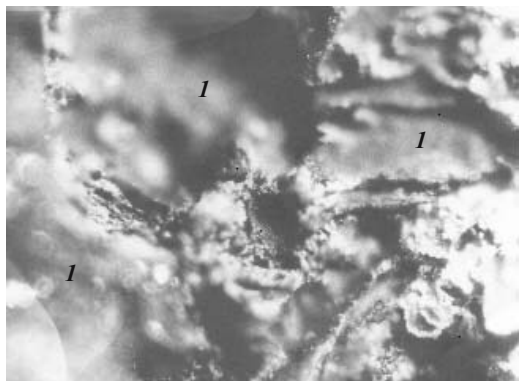


Fig. 5. Photomicrograph of a heat-treated graphite substrate (graphite scales with diffused coating material): 1) lustrless material of the coating supported on graphite flakes ($\times 750$).

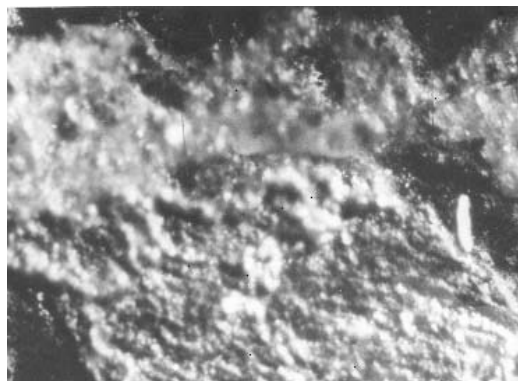


Fig. 7. Photomicrograph of a zone of incipient burn-out in the A-2-grade coating applied to a graphite substrate (cross sectional view; tested at 1973 K and holding time of 15 min).

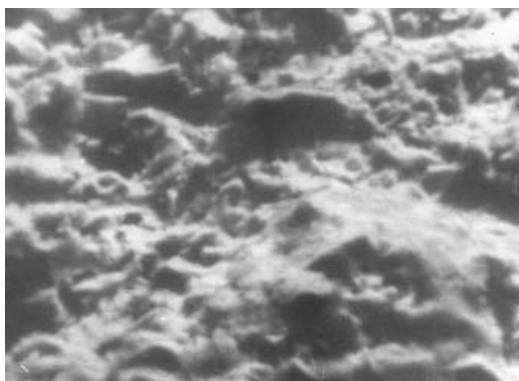


Fig. 6. Photomicrograph of a fractured coating supported on a graphite substrate (heat-treated; $\times 1600$).

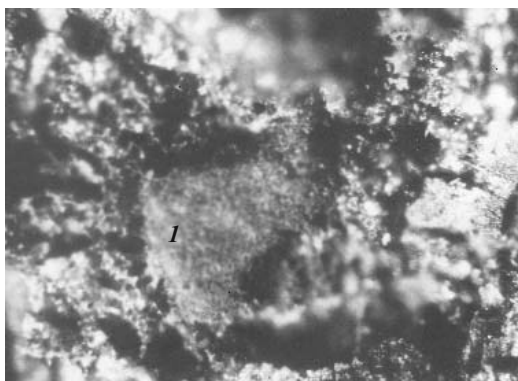


Fig. 8. Photomicrograph of a fractured graphite-to-coating contact: 1) fractured coating ($\times 3600$).

graphite substrate (Fig. 1). The coating strength in the raw state results from the polymerization of organo-silicon bonds involving the formation of $\equiv \text{Si} - \text{O} - \text{Si} \equiv$ linkages. The enhanced density and strength of the fired material comes from the intensified sintering of corundum mixes with ultradisperse SiO_2 added. When heated, the gel decomposes at a temperature as low as 773 K to yield atomic carbon and ultradisperse silicon; the latter persists in the amorphous state at above 1273 K and promotes the sintering. It has been established that the dispersity of silicon particles as silicon undergoes crystal transformation at 1273 – 1373 K is determined by conditions under which the sol was prepared. Under specifically controlled ambient conditions, β -SiC nanoparticles could be synthesized from atomic carbon and silicon monoxide [20].

Using a sol-gel technology, a dense intermediate corundum layer was developed that was reinforced with β -SiC nanoparticles and mullite whisker; this layer was an impermeable barrier for the diffusion of carbon into the oxide filler even at operating temperatures higher than 2000 K [9]. The rate of interaction between SiO_2 particles and the filler is

controlled by the uniformity of distribution of the ultradisperse particles of sol-gel compositions on the surface of the refractory filler. Depending on the thermodynamic conditions, the performance properties of the coating can be improved either by sintering or owing to the formation of new phases (Fig. 2). A heat-treatment regime was developed that permitted the buildup of a dense thermally stable structure with a specified phase composition.

It was thought of interest to study protective properties of the coatings based on self-hardening bonds and the rate of oxidation of coated graphite materials at high temperatures. The thickness of a coating is known to be a major property that determines the coating's protective efficiency and the service life of coated graphite materials. However, increasing the thickness of a coating does not necessarily improve protective properties and quality of the coating considering that adhesiveness, bending strength and other physicomachanical properties are likewise controlled by the thickness. In our case, the thickness of a coating based on self-hardening corundum mixes and organo-silicon bonds did not exceed 600 μm . The coating was applied to the surface of graphite

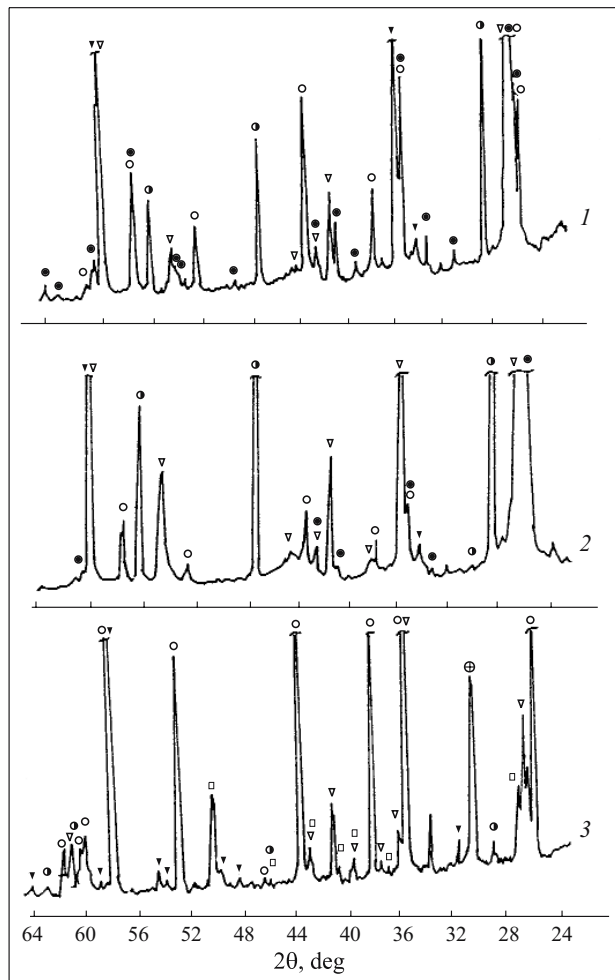


Fig. 9. X-ray diffraction patterns of a coating tested at 1973 K: 1) intermediate layer; 2) base layer; 3) fused surface layer; ○, α - Al_2O_3 ; ● mullite; ▽ β -SiC; ● Si; ▼ carbon; □ quartz; ⊕ stishovite.

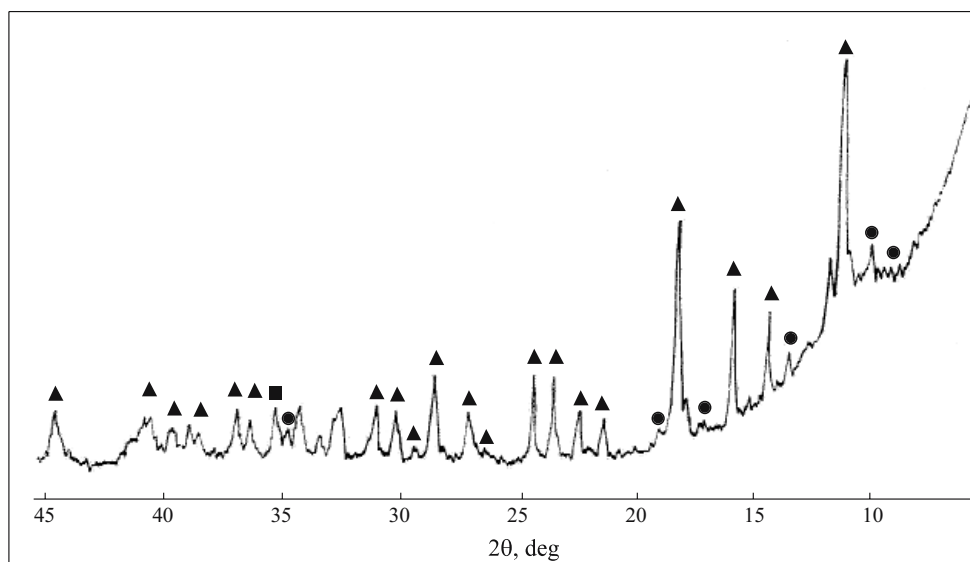


Fig. 10. X-ray diffraction pattern of the C-3-grade coating: ▲ Al_2O_3 ; ● Si_2ON_2 ; ■ SiC.

specimens of different grade. The best adhesion of sol-gel-bonded coatings was found with siliconized graphite. The coatings were tested for protective properties using siliconized specimens. The tests were conducted using a hot pressing technique in a freely circulating air.

The base layer had a thickness of 0.5 – 0.7 mm, it exhibited a dense structure and was mainly composed of corundum and mullite. Mullite formed a needle-like network on the corundum grains. Fine mullite grains 1 – 2 μm across incorporated between corundum grains and on the surface were observed (Figs. 2 – 4). The coating material was deeply penetrated into structural imperfections of the graphite specimen, the coating-to-graphite contact was quite tight so that in specimens tested for adhesiveness the coating material remained stuck to the graphite flakes. The diffused material, lustreless in appearance, is found spread over the graphite flakes and in the pores between them (Fig. 5). Fine newly formed crystals were also visible embedded in the coating.

The particles prepared by sol-gel method were observed to diffuse into microcracks and other microscopic imperfections of the graphite specimen, which increased the adhesiveness of coating, especially after thermal treatment (Fig. 6) owing to the formation of SiC and mullite. SiC (formed from the bond constituents) and mullite (produced by the interaction between SiO_2 and bond constituents) promoted the densification of the intermediate layer [19]. Mullite occurred as needle-like species in the structural imperfections, in the intermediate layer, and in the bulk of the coating, which resulted in an increase in adhesive strength, decrease in thermal linear coefficient of expansion (TLCE) of the coating, and increase in its thermal stability.

The best resistance to oxidation, as shown by test results, was found in C-3-grade coatings which, well-sintered at 1673 K, were free of glassiness and retained high adhesiveness to siliconized graphite at high temperatures.

The C-3-grade coating, when sintered, forms a dense intermediate layer (see Fig. 6); this layer, owing to its high adhesiveness to siliconized graphite, prevents diffusion of carbon from the graphite substrate into the base layer and thereby inhibits the diffusive oxidation graphite, which makes the siliconized graphite resistant to oxidation (for a short period of time, though) even at temperatures as high as 2023 – 2063 K. At temperatures below 2023 K, the coating showed no detectable damage or local burns. The incipient burning-out was apparent at temperatures above 2023 K (Fig. 7).

Subjected to the long-term testing at 1973 K, the C-3 coating was retained over the entire surface of the test specimen (Fig. 8).

A petrographic study of the coating and its contact with graphite at 1973 K has revealed several features. Diffusion of the coating material into the graphite bulk extended to a depth of 300 μm (via lattice and structural imperfections). Pores filled with fused material could be observed in the contact zone. A dense intermediate layer a few microns in thickness was clearly visible at the graphite and coating boundary. A specified phase composition of this layer could be controlled during sintering. During service, the base layer of the coating underwent mullitization. A network of mullitic needles sizing 1–2 μm was seen spread over the grains and bonding mix; which added to the strength and heat resistance of the material. The amount of carbon burn-out in graphite components coated with a thin layer of corundum and sol-gel composite at 1973 K (holding time 15 min) did not exceed 1%; no oxidation zone was observed.

As was noted above, the C-3 coating gave a high resistance to oxidation below 2023 K. Considering that the temperature control during the testing was done by measuring the temperature of the side surface of the coated graphite specimens, the actual temperature was underestimated by 100–200 K at the least. Since the refractory putty, when heated, has a luminosity smaller than that of siliconized graphite, the actual operating temperature might be 2123–2223 K.

Reasons for the occurrence of “dark spots” on the surface of coatings were also considered. The dark spots were observed to emerge in specimens tested at high temperatures (2023 K) and holding times within 10 min; this effect is associated with an air layer trapped between the loosely adhered coating and a portion of the substrate surface “dotted” with structural imperfections (see Fig. 7). To remove the flaw, the

machined graphite surface should be carefully finished before applying the coating. The burn-outs may come from two reasons: first, because of the poor air-blast cleaning of the graphite components, the remaining fragments or graphite flakes are prone to a faster oxidation during heating, which leads to the accumulation of gases CO and CO₂; these promote further oxidation of the graphite material and thus facilitate mullitization. Second, as graphite undergoes oxidation, a high gas pressure may be produced beneath the coating sheath, which is favorable to the transition of SiO₂ (a constituent of the sol-gel composition) to stishovite; this has a density higher compared to other SiO₂ modifications. SiO₂ thus present in the coating causes an increase in porosity and, in places, a local fusion and emergence of a transparent material; the coating thins down to a thickness of 180–200 μm , and “dark spots” develop, the nuclei for coming burn-outs. The latter version has been borne out by x-ray phase analysis (Fig. 9).

Thus, the newly developed coatings provide sufficient protection from oxidation. The use of sol-gel compositions and mechanochemical activation promises further advances in exploring the range of protective coatings for graphite and carbon-containing materials.

Sol-gel impregnation of the first (ground) C-3-layer in the A-grade multiple coating makes the intermediate layer more compact, which improves the resistance to oxidation. Results for C-3 coating and A-grade multiple coating tested for phase composition are given in Figs. 10 and 11. The test results have shown that the newly developed C-3-and A-grade coatings can be used to protect graphite components from oxidation. The coatings were applied to the rotor blade of a turbine and to structure components (refractory plates and cylinders) and then heat-treated under specified conditions.

TABLE 1. Test Results for Single-Layer and Multiple-Layer Coatings Based on C-3-grade Composite

Composition label	Testing temperature, K	Holding time, min	Features observed on the surface of coating tested
C-3/1	1833	3	No change
	1913	3	No change
	2003	3	No change
	2023	3	Single burn spots
	2063	3	Multiple burn spots
	2213	3	Incipient assemblage of burn spots
	2223	3	Denudation ($\geq 50\%$) of graphite surface; vitrification of the rest of surface
C-3/4	1973	15	Good coating adhesion; coating retained over the entire surface of specimen, however, dotted with multiple burn spots of darker color
A-1	1873	10	Coating integrity retained
A-3	1923	30	Coating integrity retained; in places stained with spots of milky color
A-2	1973	10	With occasional burn spots
A-4	2023	10	The same

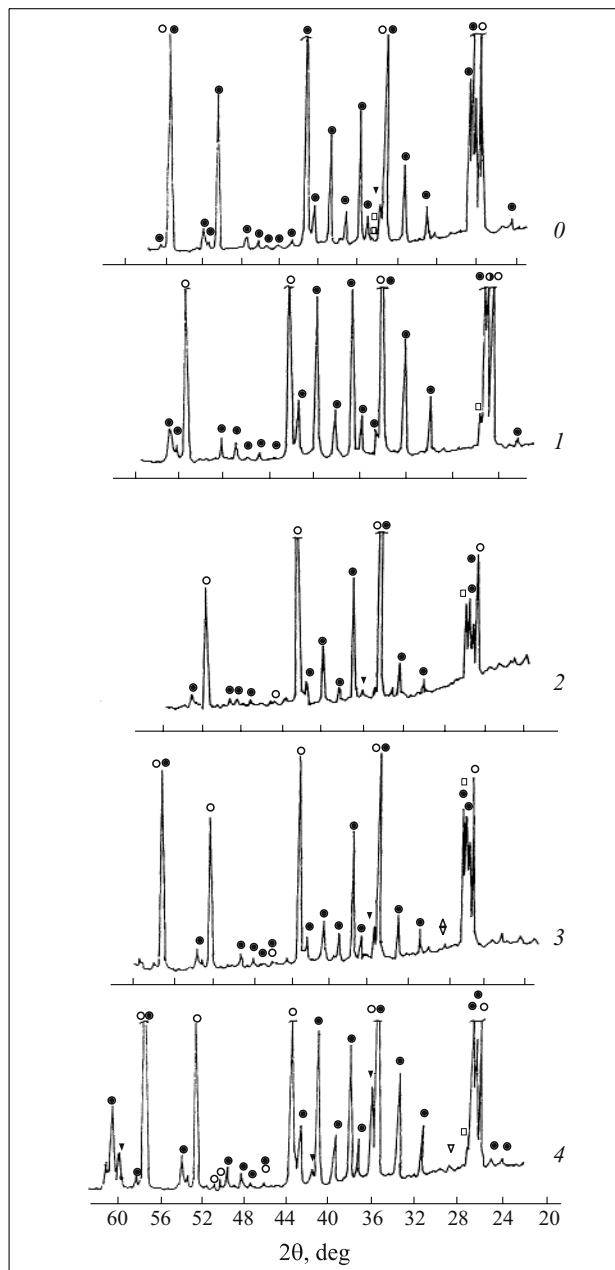


Fig. 11. X-ray diffraction patterns of a multiple-layer coating subjected to heat treatment: 0) initial composition; test temperature, K: 1) 1973; 2) 1923; 3) 1973; 4) 2023; ○) α - Al_2O_3 ; ●) mullite; ▼) SiC; □) quartz; ▽) C; ◇) Si.

Thus, the theoretically predicted low-temperature synthesis of β -SiC from electrofused corundum mechanically activated by silicon alkoxide under argon or air has been verified experimentally. The newly-developed coatings and technology for their preparation provide effective protection of siliconized graphite from oxidation at temperatures up to 2023 K (Fig. 12).

Thus, using a sol-gel method in the technology of a self-hardening refractory putty, a heat-resistant coating for

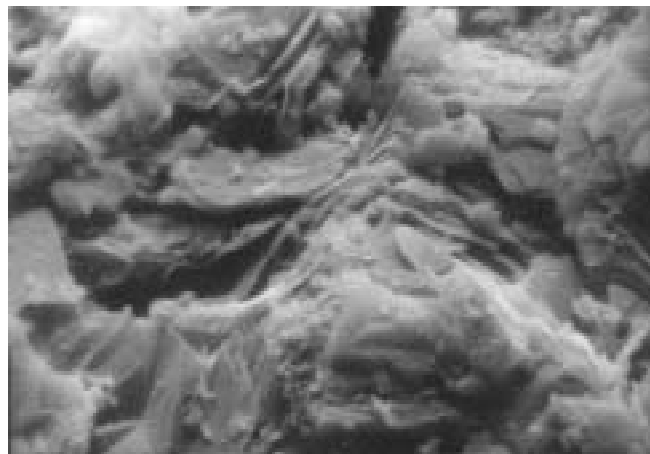


Fig. 12. Fracture surface of the contact layer (tested at 2023 K; $\times 20,000$).

protection of siliconized graphite at temperatures as high as 2023 K. Relevant test results are given in Table 1.

For protection of large-size graphite electrodes, a range of nonfired composites based on modified corundum have been proposed. When in service, they convert to a molten material which cements the surface of a coating and enhance thereby the adhesion of coating to a graphite electrode. The results of a weight-loss study carried out on graphite electrodes have shown that composition $\text{Al}_2\text{O}_3 - \text{BaO} - \text{SiO}_2$ was the best suited for protection of electrodes owing to the fact that at temperatures below 1100 °C, the weight loss of a nonfired coating did not exceed 1% (degradation of the sol-gel composition is involved in the process). At temperatures above 1100°C, initially a melt ($\text{Al}_2\text{O}_3 + \text{ultradisperse SiO}_2$) is produced, and at still higher temperatures □ a composite $\text{Al}_2\text{O}_3 - \text{BaO} - \text{SiO}_2$ is formed which prevents the coating from failure and the electrode surface from flaking; using this technique, the service life of electrodes could be extended by 35 – 40%.

To briefly summarize, the following conclusions can be drawn:

to reduce oxidation of graphite components, a range of methods have been proposed; of these, the best suited is the use of coatings with a thin intermediate layer to prevent diffusion of carbon from the graphite component into the oxide filler of the coating;

heat treatment of coated graphite components is typically carried out in an inert atmosphere; when needed, a combined atmosphere can be used containing air to produce a densely sintered coating in the early stage of the process;

the newly-designed coatings make it possible to increase the heat resistance of graphite components by a factor of 1.5 or even more.

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