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SELF-HARDENING COATINGS FOR PROTECTION OF GRAPHITE PRODUCTS FROM OXIDATION

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Results of testing coatings for silicided graphite that are based on a self-hardening mixture (Al_2O_3 powder modified with silicon alkoxide and ethyl silicate binder) are presented. The dense intermediate layer created, reinforced with mullite and SiC inclusions that resulted from mechanochemical reactions and firing, is shown to provide high resistance to oxidation for graphite up to 2003 K.

The increase in the production of structural ceramics with special properties is attributable to the growing requirements of different branches of industry, including requirements of new technologies. The requirements on the durability of graphite structural materials grow continuously.

Graphite is a material possessing unique chemical and physicomechanical properties: inertness in aggressive environments, high thermal stability, high heat conduction, high strength, etc. [1, 2]. Wider application of graphite is limited by its low refractoriness and erosion in gas flows. Protective coatings are designed to increase its refractoriness and resistance to oxidation [3–7]. The most effective ones are multilayer coatings of silicon carbides and nitrides, molybdenum and tungsten silicides, and zirconium and hafnium dioxides. Formation of carbide sublayers reduces the difference between the temperature coefficients of linear expansion (TCLE) of the graphite base and the coating, which diminishes the thermal-stress level and the possibility of destroying the integrity of both the base and the coating. The refractoriness and heat resistance of the coating depend not only on its composition and method of production but also on the quality of the initial carbon material [7].

The most efficient way of increasing the strength of the bond between the oxide coating and graphite is the use of SiO_2 oxide layers, which form dense carbide layers at high temperatures of interaction with graphite [8]. Participation of the carbon of the substrate in carbide synthesis is undesirable since it results in disruption of the continuity of the graphite structure and in erosion-caused wear. The paper [7] describes impregnation of the sublayer in order to decrease its porosity. This recommendation was used in developing coatings that contain sol-gel compositions.

The present paper describes results of testing the resistance to oxidation of graphite products on whose surface self-hardening coatings based on Al_2O_3 modified with an organoelemental component and ethyl silicate binder were applied.

It is established that each type of graphite requires a special approach in designing such coatings and technologies for their application. Special attention should be paid to preparing the surface of graphite parts and their heat treatment before applying the coating.

Electrocorundum was used in designing the coatings. To modify Al_2O_3 , silicon alkoxide was used, and ÉTS-32 served as the ethyl silicate binder. ÉTS-32 was hydrolyzed in an aqueous acid medium without organic solvents. Silicided and nonsilicided PROG-2400 graphite was used as the graphite substrate. Coatings of thickness 0.6–0.7 mm were applied manually with a brush on the surface of laboratory samples, which were then fired by a specially developed procedure. The maximum firing temperature did not exceed 1653 K. The coatings were tested on a hot-molding press in freely circulating air. The temperature was measured with an OPPIR-2 pyrometer (measurement accuracy ± 298 K).

The sol-gel process improves the adhesion of the coating to the substrate and produces diffusion of the ultradispersed elemental particles comprising the sol-gel composition to a depth of 10–40 μm before hardening. Good wettability of the substrate by the self-hardening mixture and its uniform distribution over the surface of the carbon material that requires protection should provide good coverability and good adhesion of the coating to the substrate in the absence of interaction between the carbon of the substrate and the coating components under sintering.

In order to improve the protective properties of coatings based on Al_2O_3 and ethyl silicate binders we planned β -SiC synthesis in an intermediate layer made up of the components of the self-hardening matrix. Intensification of β -SiC synthe-

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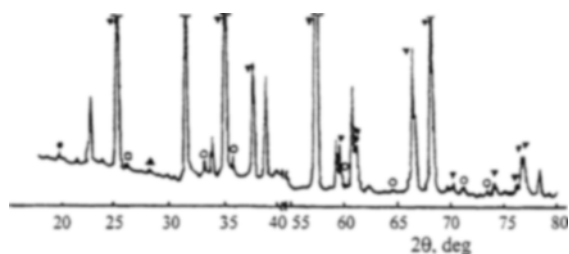


Fig. 1. Diffractogram of modified electrocorundum after grinding with an addition of silicon alkoxide in a ball mill for 2 h: \blacktriangledown) α - Al_2O_3 ; \circ) SiC; \bullet) Si_2ON_2 ; \square) mullite; \blacktriangle) Si.

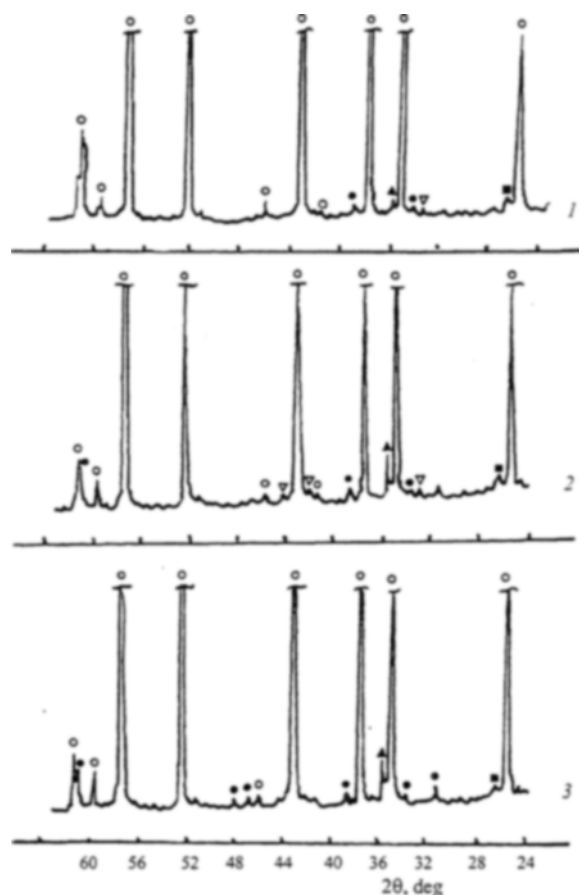


Fig. 2. Diffractograms of modified electrocorundum after firing at 1273 K in air (1, 2) and in argon (3). Mass fraction of the addition: 1) 1%; 2) 3%; 3) 1%: \circ) Al_2O_3 ; \bullet) mullite; \blacktriangle) SiC; \blacksquare) quartz; ∇) β - Al_2O_3 .

sis was achieved by using electrocorundum modified with silicon alkoxide. β -SiC was identified by radiography in the modified electrocorundum after grinding with an addition of silicon alkoxide (Fig. 1). After firing the modified electrocorundum in different environments at 1273 K the intensity of the β -SiC peak grows with increase in the amount of modi-

fying addition (Fig. 2). As a result of grinding Al_2O_3 with silicon alkoxide the corundum grain surface becomes amorphous, defects are accumulated in the grain structure, $\text{Si}(\text{OC}_2\text{H}_5)_4$ is destroyed mechanically, and amorphous alumina and carbon clathrates are formed in it, and furthermore, due to mechanochemical reactions the grinding process results in the formation of a metastable mullite phase and SiC [9–12]. After annealing Al_2O_3 defects in firing the modified electrocorundum almost no mullite-like phase is identified, and SiC nuclei, once formed, grow with increase in the heat-treatment temperature, especially in a protective environment that prevents oxidation of SiC.

The coatings developed have a high resistance to oxidation. Unlike coatings based on other oxides, a coating based on modified corundum and ethyl silicate binder does not vitrify after firing, and good adhesion to the graphite sample surface is observed. In firing a coating based on modified Al_2O_3 and the sol-gel composition an intermediate layer is formed on the graphite surface that reliably holds the main layer of the coating to the surface of silicided graphite. This provides resistance to oxidation at 1900–2000 K, which meets the service requirements on graphite parts.

The modified- Al_2O_3 coating was taken as the base for multilayer coatings. In the course of application, firing, and service the latter diffuses into a graphite material of relatively low density to a depth of 300 μm . For the contact zone the presence of single pores filled with an aluminosilicate melt is typical. After service at 1973 K for 15 min a denser intermediate layer of width 3–8 μm becomes clearly visible at the border between the coating and the graphite surface. In the course of testing, three zones different in phase composition and structure are formed: the intermediate layer at the contact with the silicided-graphite surface, the main layer, and the dense surface layer (Fig. 3)

The main layer of width 0.5–0.7 mm has a dense structure and consists mainly of corundum and mullite. The mullite covers the corundum grains with a needle mesh. On the surface of the corundum grains and between them in the main layer small grains (1–2 μm) of mullite are formed. The contact of the coating and the graphite after the tests is so strong that during the adhesion testing the coating is removed together with layers of graphite. The coating penetrates deep into structural defects of the graphite sample. The coating, having diffused into these defects before the firing, covers graphite scales and fills the pores between them, making the graphite material denser. The sol-gel composition, diffusing into microcracks and other microdefects of the graphite sample, increases the strength of adhesion of the coating to the graphite immediately after application, and after heat treatment this becomes more evident due to the appearance of phases (SiC and mullite) raising the heat resistance of the coating. The formation of SiC and mullite contributes to a higher density of the intermediate layer and increases its refractoriness. The formation of mullite in the shape of thread-like crystals both at defect sites of the graphite sample and in

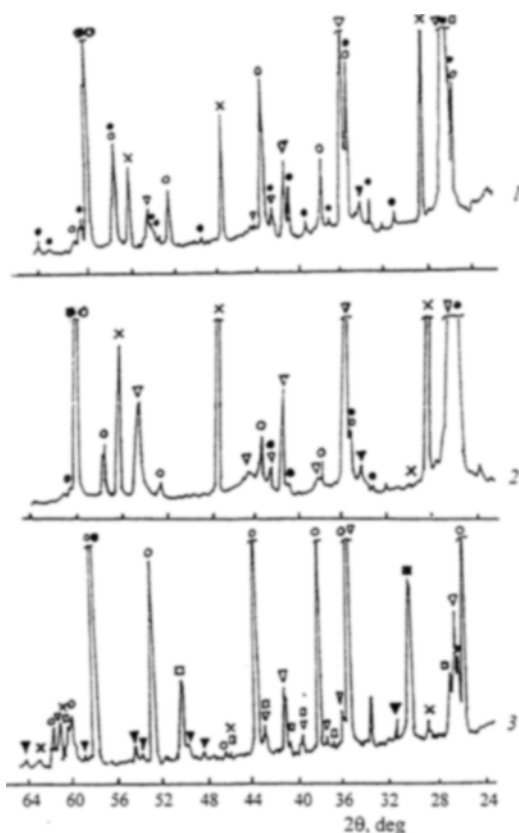


Fig. 3. Phase composition of a coating after testing at 1973 K: 1) intermediate layer; 2) main layer; 3) vitrified part of the coating surface layer: ○) α - Al_2O_3 ; ●) mullite; ▽) β -SiC; ×) Si; ▴) carbon; □) quartz; *) stishovite.

the main-layer material of the coating contributes to a reduction in the coating TCLE, thus increasing its heat resistance.

As was noted above, a coating based on modified Al_2O_3 and the sol-gel composition has a high resistance to oxidation up to 2000 K, which is confirmed by the stability of the phase composition of the coating during heat treatment at different testing temperatures (Fig. 4). In testing the coating the temperature was monitored by the temperature of the side surface of the graphite samples covered with a layer of the coating tested, and thus, the temperature recorded was at least 100–200 K lower than the actual one, since the coating has significantly less illumination when heated than silicided graphite.

The use of mechanoactivated corundum filler and ultradispersed amorphous alumina of sol-gel compositions in coatings not only intensifies sintering of the material during heat treatment but also produces a sublayer whose density and heat resistance grow in connection with β -SiC and mullite synthesis. Their formation is accompanied by an increase in volume compared to the volume of the initial components and prevents interaction of the amorphous alumina with the graphite of the sample coated. The dense intermediate layer on the silicided-graphite sample surface prevents passage of the carbon of the substrate into the coating and its oxidation during service.

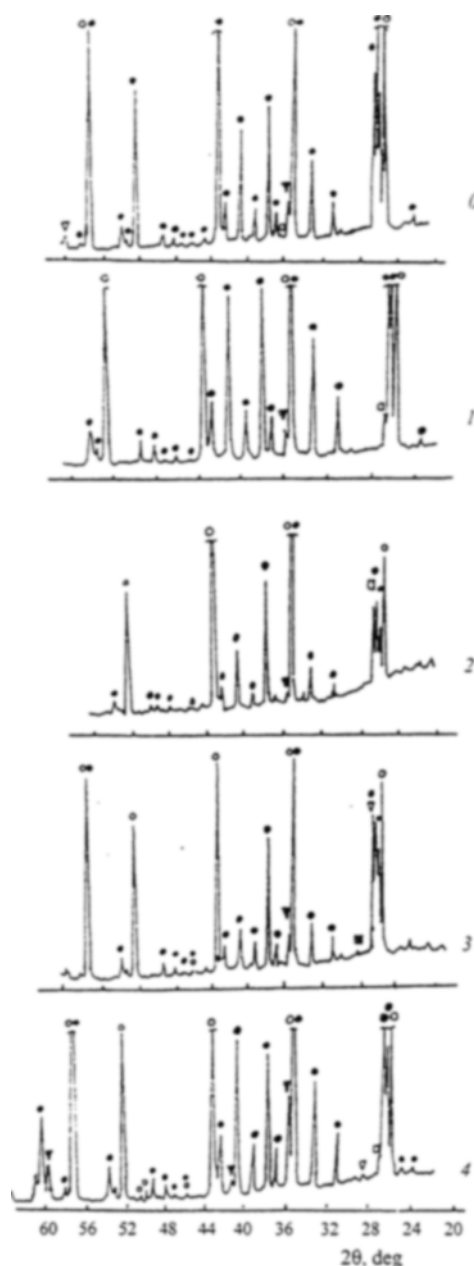


Fig. 4. Changes in the phase composition of a multilayer coating in heat treatment at different temperatures, K: 1) 1873; 2) 1923; 3) 1973; 4) 2023; 0) initial composition; ●) mullite; □) quartz; ▽) SiC; ▴) C; *) Si.

The reasons for the appearance of dots (Fig. 5) on the coating surface in the course of testing at temperatures above 2023 K for 10–15 min were investigated. The dots relate to an air interlayer under the coating resulting from a less tight fit at defect sites on the sample surface. This points to the need for more careful preparation of the graphite sample surface after machine treatment before applying the coating. The appearance of burnouts may occur for two reasons. First, with poor pneumatic treatment of graphite articles the remaining debris or graphite scales are oxidized in heat treatment of the

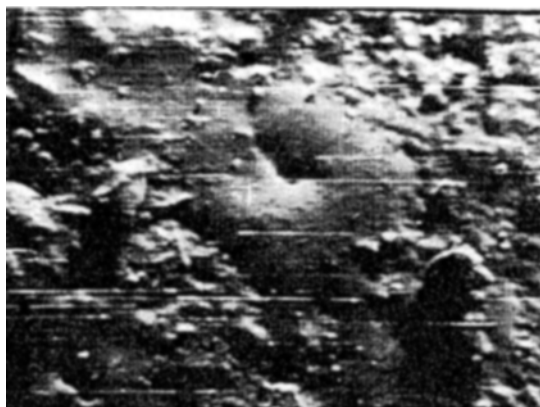


Fig. 5. Exterior surface of a coating after testing at 2023 K; $\times 700$.

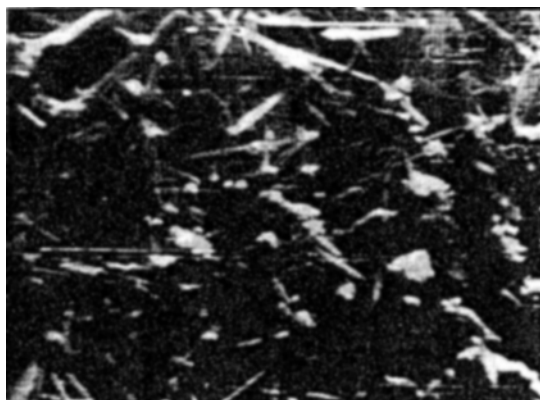


Fig. 6. Surface of breaking away of a coating that contains the combined sol-gel binder (aluminum oxychloride-ethyl silicate) from the graphite substrate; $\times 3000$.

coating. This results in accumulation of CO and CO₂ gases, whose presence under the coating causes oxidation of the carbon in the sample and facilitates formation of mullite in the form of threadlike crystals (Fig. 6); the coating flakes from the graphite sample surface. Second, in graphite oxidation a high pressure arises under the coating, which facilitates conversion of SiO₂ of the sol-gel composition that is not bound in the new formations into stishovite. Its density is higher than that of other SiO₂ modifications, which causes an increase in the coating porosity, vitrification of the coating at these sites, and the appearance of transparent portions. The coating thickness diminishes to 180–200 μm , and the dots appear, indicating sites of future burnouts of the coating. The second assumption is confirmed by x-ray phase analysis data.

The exterior surface of a coating after testing at 2023 K is shown in Fig. 5. When using an Al₂O₃–SiO₂ sol-gel composition as the binder the diameter of the burnouts formed is around 20 μm . Use of the composition resulted in synthesis of large amounts of threadlike mullite crystals, which affected negatively the resistance of the graphite pieces to oxidation.

Impregnation of the first applied layer based on modified corundum in multilayer coatings with the sol-gel composition contributes to an increased density of the intermediate layer, which gives positive results in testing the resistance to oxidation. The optimum-composition coating thickness after testing of silicided samples at 2023 K was 380–500 μm , and under the dots it was 150–180 μm ; burnouts were not present.

Thus, synthesis of β -SiC in the intermediate layer of the coating at low temperatures in the corundum mechanoactivated with a silicon alkoxide addition is confirmed experimentally. The developed coating provides high resistance to oxidation for silicided graphite up to 2023 K. The coatings developed can be used to protect from oxidation products made of other types of graphite as well, e.g., electrodes.

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