PROTECTION OF GRAPHITE
AND GRAPHITE-CONTAINING MATERIALS FROM OXIDATION

G. D. Semchenko, I. Yu. Shuteeva, O. N. Slepchenko, and L. A. Angolenko


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 in tended 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...
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-consuming 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: Al2O3, 1923 K; BeO, 2253 K; MgO, 1923 K; SiO2, 1753 K; ZrO2, 2253 K; MgO · Al2O3, 1523 K, etc. Of interest are also combinations of carbon with BaO, Cr2O3, 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 SiO2. The aluminosilicate bond fails to provide full protection to graphite from oxidation because of the increased porosity coming from the interaction between carbon and SiO2. 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 Si + C → β-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; B4C, 1373 K, and MoC, 1173 K. It was shown...