Silicon carbide coatings substantially raise the oxidation resistance of graphite at high temperatures, and may therefore often be recommended as a means of protecting the surface of graphite against oxidation. Of particular interest are nonporous coatings, which may be deposited from the gaseous phase.

Investigations of the formation of silicon carbide [1-4] and of the silicon-carbon-boron system [5-7] during the deposition of the elements from the gaseous phase have been reported in the literature. The majority of these investigations were concerned with the semiconducting and mechanical properties of silicon carbide and its alloys; and the influence of temperature, process duration, and composition of the gaseous mixture on the kinetics of deposit formation has not been examined adequately. The protective properties of silicon carbide coatings at high temperatures have also received little study.

The oxidation of silicon carbide powder was studied in [8], where it was established that green silicon carbide has high oxidation resistance. However, the authors' own investigations demonstrated that coatings from this carbide are incapable of protecting the surface of graphite against oxidation. Little is known of the adhesion of such deposits to substrates, their thermal shock resistance, etc.

In the present investigation, a study was made of the formation of a coating by silicon carbide on graphite, and some properties of the resulting material were determined. Coating deposition on graphite was performed from a gaseous mixture of silicon tetrachloride, hydrogen, and benzene. Figure 1 shows a diagram of the apparatus used for the deposition of silicon carbide coatings.

Hydrogen, produced electrolytically in the apparatus 1, passes through the vessel 2 with concentrated sulfuric acid, where water vapors are removed from it. The rate of flow of hydrogen is measured with the gauge 3. For the removal of oxygen, the hydrogen flows through the furnace 6, which contains magnesium shavings, preheated to a temperature of 650°C. After the removal of oxygen, the hydrogen passes above benzene and then above silicon tetrachloride, forming a mixture with vapors of these compounds. To obtain the required benzene and silicon tetrachloride concentrations in the gaseous mixture, the temperatures of these compounds were chosen with the aid of curves showing the influence of temperature on the concentration of silicon tetrachloride and benzene (Fig. 2a and b). These curves were plotted experimentally by measuring the amounts of silicon tetrachloride and benzene picked up at various temperatures and hydrogen flow rates for the same evaporation surface area (28 cm²). The temperatures of silicon tetrachloride and benzene were maintained constant during experiments by means of thermostats.

The hydrogen, silicon tetrachloride, and benzene mixture obtained in this manner was fed into a quartz tube, which contained a graphite specimen and was located in the inductor of a high-frequency unit. As a result of heating, silicon carbide formation reactions took place on the specimen surface. The table lists values of the isobaric potential (ΔZ) of some reactions, calculated for compounds in a standard condition over the temperature range 1200-2000°C. The numerical values of ΔZ show that Nos. 1-3 and 9 are the most likely reactions of silicon carbide formation on the graphite surface at temperatures of 1700-1800°C.
It was established by thermodynamic calculation and experimentally that silicon carbide formation is only possible in the presence of hydrogen in the silicon tetrachloride and benzene mixture. When hydrogen is replaced by helium, it is impossible to obtain silicon carbide. This is due to the fact that hydrogen plays an extremely important part in these reactions as a reducing agent.

One of the principal parameters in the process of silicon carbide preparation is the ratio of the silicon tetrachloride and benzene concentrations. It was established by the authors that silicon carbide can be produced when the ratio of the silicon tetrachloride and benzene concentrations is not less than 12:1. In such a case when oxygen is present in the reaction space, green silicon carbide may be obtained.

Oxidation-resistance tests have shown that green silicon carbide coatings offer little protection to the graphite surface at high temperatures. When the surface of green silicon carbide coatings was examined under the microscope, it was found that these coatings were very porous (Fig. 3). The presence of pores explains why these coatings are incapable of protecting the surface of graphite at high temperatures.

In the absence of oxygen in the reaction space, dark silicon carbide forms on the specimen surface. It was found by x-ray structural analysis that both carbides have a ZnS-type cubic \( K_4 \) structure with the lattice parameter \( a = 4.357 \) Å.

The composition and properties of the coating depend on the ratio of the silicon tetrachloride and benzene concentrations in the gaseous mixture. Thus, at concentration ratios smaller than 12:1, coatings consisting of a mixture of pyrographite and silicon carbide are produced. It will be seen from Fig. 4 that