CERTAIN FEATURES IN THE OXIDATION OF CARBON-GRAPHITE MATERIALS

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The features of interaction between synthetic graphites and oxidizing agents are examined, with a method proposed for separating the effect of physical and chemical factors. Experimental data are presented on the differentiated determination of graphite mass-loss rate on oxidation with the oxygen in the air.

Synthetic graphites are used extensively in industry; however, their inadequate resistance to oxidation limits the areas of application. The increasing role of synthetic graphites in new branches of engineering has stimulated the appearance of a considerable amount of work on the interaction of graphite with oxidizing agents [1, 2]. Unfortunately, in much of the research into the kinetics and mechanism of the oxidation reactions absolutely no consideration is given to the features of the structure of synthetic graphites, imposed by the techniques of their fabrication, although the influence of micro- and macrostructures in the graphite on interaction with oxidizing agents is undisputed [3].

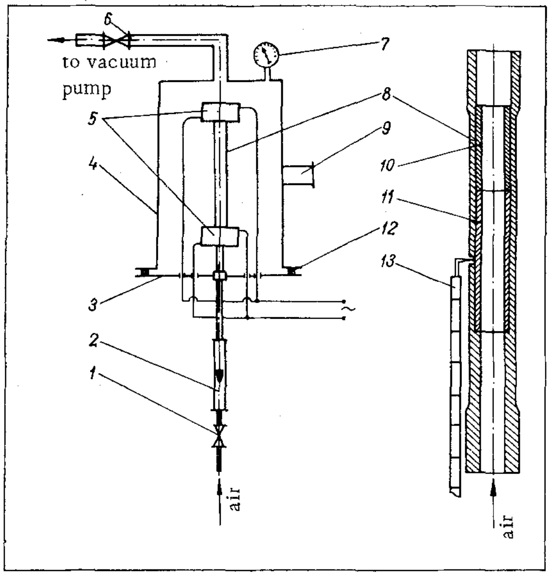

Fig. 1. Experimental apparatus: 1 and 6) vane; 2) rotameter; 3) tray; 4) vacuum chamber; 5) current supply; 7) vacuum manometer; 8) heater; 9) viewing window; 10) guard insert; 11) sample; 12) packing; 13) thermocouple.

Synthetic graphites are derived by binding a coke filler with the coke formed in the carburization of coal-tar pitch which serves as the binder in the subsequent graphitization of the semifinished product [4], with the coke residue of the binder not distributed uniformly among the filler particles, but rather forming bridge bonds between them [5]. The interaction of the synthetic graphites with the oxidizing agents takes place primarily through the oxidation of the binding bridges [6], causing the crumbling of the nonoxidized filler particles and an increase in the actual reaction surface.

An attempt is made here separately to determine the effect of physical and chemical factors on the rate of mass loss in synthetic graphites on interaction with oxidizing agents.

The basic diagram of the experimental installation is shown in Fig. 1. The test specimen 11, made in the form of a hollow cylinder with $\varnothing\ (20 \times 16) \times 110$ mm is placed into heater 8 made of silicided graphite. The heating and cooling of the specimen was accomplished in vacuum chamber 4 in which the vacuum was created by means of a VN-1 mg vacuum pump. Temperature is measured with thermocouple 13 or the OPPIR-017 optical pyrometer through inspection hatch 9. The oxidizing agent is fed into the reaction space through rotameter 2. The specified pressure is established in the vacuum chamber by means of throttling device 6, with the pressure monitored by means of a vacuum pressure gauge 7. The power supply unit consists of an OSU-40 power transformer and two ROT-25/05 autotransformers. The installation makes it possible to carry out experiments accurate to ±10% over a wide interval of pressures ($\lesssim$ atmospheric) in the temperature range 600–2000° C. In this investigation the graphite was oxidized at atmospheric pressure in a stream of air moving at a speed of about 0.02 m/sec.

Three forms of synthetic graphite were selected for the study, differing in their granulometric filler composition and in density.

In the process of oxidizing a machine-finished surface, which is a necessary condition for current methods of determining oxidation rates in synthetic graphites, W attains a constant value within a specified time interval (Fig. 2). The graphites were oxidized at the transition temperature (of the oxidation process) between the extrakinetic and the extradiffusion regions, i.e., at about 900° C under the conditions of the experiment. The finishing of the specimen surface by oxidation at lower temperature is undesirable because of the significant drop in graphite strength [7] as a result of the oxidation of the binding bridges between the filler particles during interstitial reactions. We see from Fig. 2 that the time of entry into the steady oxidation regime is directly proportional, while the quantity W = const is inversely proportional, to the density of the graphite and the coarseness of its filler. It should be noted that in this case the power effect of the oxidizer on the reaction surface is insignificant. On interaction of synthetic graphites with a high-speed gas flow, aerodynamic forces [8] act on the protruding grains of the filler, and these forces may alter the nature of the relationship between W and the structural characteristics of the graphite.

We see from Fig. 3 that the function $W = f(T)$ in Arrhenius coordinates in the extrakinetic region of reaction is rectilinear in nature. This function is generally used to determine the kinetic characteristics of graphite reactions with oxidizing agents [1, 2]. In the meantime, the total rate of graphite mass loss in oxidation may be represented by the expression

$$W = W_1 + W_2 + W_3, \qquad (1)$$

where W_2 is defined by the value of the total pore surface accessible to the oxidizing agent, while W_3, as shown in Fig. 2, is a function of the granulometric composition of the filler and of the graphite density, i. e., two components of W characterize the structure of the synthetic graphites, and not the chemical properties of the graphite. This circumstance is apparently the fundamental reason for the extremely contradictory results of kinetic investigations of graphite reactions with oxidizing agents, these investigation having been carried out on specimens of various grades of synthetic graphites.

On the basis of the foregoing, the determination of the kinetic characteristics of the chemical reaction of graphite with oxidizing agents on the basis of the rate of mass loss in the carbon-graphite material on oxidation must apparently be recognized as invalid. The determination of the true value of the apparent energy of activation for the chemical reaction of carbon and graphite with oxidizing agents is of considerable scientific and practical interest.

It follows from (1) that when $W_2 = 0$ and $W_3 = 0$, then $W = W_1$. This condition is satisfied by the oxidation of a graphite which has in its composition no grains of filler with binding bridges between them, exclusively in the extrakinetic oxidation regime. The latter is possible in the absence of through porosity in the graphite. Pyrographite [9] satisfies the imposed requirements. It is virtually impermeable to gas [10] and represents a monolith exhibiting a density approaching the theoretical.

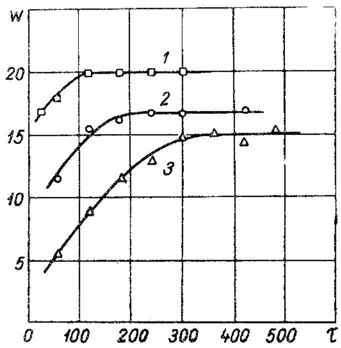

Fig. 2. Influence of time of oxidation by oxygen from the air on rate of graphite mass loss (τ, sec; $W \cdot 10^3$, kg/m^2 sec): 1) size of filler −0.15 + 0 mm, density ~$1.65 \cdot 10^3$ kg/m^3; 2) −1.2 + + 0 mm, density ~$1.65 \cdot 10^3$ kg/ /m^3; 3) −1.2 + 0 mm, density ~$1.85 \cdot 10^3$ kg/m^3.

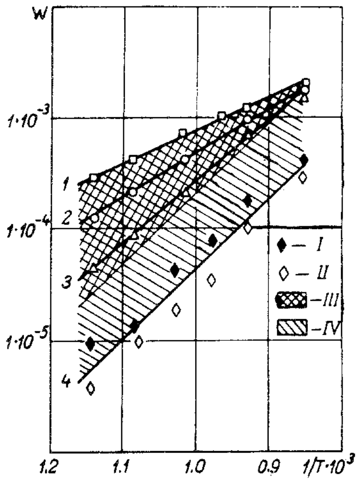

Fig. 3. Influence of temperature on rate of graphite mass loss with with oxidation by oxygen from the air ($\frac{1}{T} \cdot 10^3$, °K^{-1}; W, $kg/m^2 \cdot sec$): 1, 2, 3) total rate of graphite mass loss (respectively, size of filler −0.15 + 0 mm, density ~$1.65 \cdot 10^3$ kg/m^3; 1.2 + 0 mm, density ~$1.65 \cdot 10^3$ kg/m^3; −1.2 + 0 mm, density ~$1.85 \cdot 10^3$ kg/m^3); 4) rate of chemical reaction of graphite; rate of chemical reaction of oriented graphite crystals I) along the *a*-axis; II) along the c-axis; III) rate of mass loss due to intrapore reaction; IV) increase in rate of mass loss due to crumbling of non-oxided filler particles and increase in actual reaction surface.

The rate of chemical reaction for a graphite with an unordered orientation of crystallites, which is characteristic of synthetic graphites obtained by the methods of electrode technology, is defined as the arithmetic mean of the rates of the chemical reaction of graphite in various crystallographic directions

$$W_1 = 1.5 \cdot 10^2 \exp\left(-\frac{29500}{RT}\right). \qquad (2)$$

It is difficult in the experimental determination of W_2 to establish with acceptable accuracy the number of micropores whose surface according to [11] offers no access to the oxidizing agent. Direct experimental determination of W_3 also involves considerable difficulties.

Let us demonstrate the possibility of analytical determination of W_2 and W_3 on the basis of the experimental data for W and W_1.

Above a certain temperature, W is limited by the rate at which the oxidizer is supplied, as a result of which the reactant enters into interaction with the graphite only on the external surface, without diffusing into the pores. It follows from (1) that when $W_2 = 0$,

$$W_3 = W - W_1. \tag{3}$$

The quantity W_3 is a function of the rate of filler particle stripping, defined by W_1, the granulometric composition of the filler and the density, constant for a given graphite grade. Therefore the function $\ln W_3 = f(1/T)$ can be represented by a straight line drawn from the point of intersection of the oxidation regime from the extrakinetic to the extradiffusion region, parallel to the straight line of the function $\ln W_1 = f(1/T)$.

In the extrakinetic reaction region the amount of oxidizer is above the stoichiometric, as a result of which the excess oxidizer diffuses into the graphite pores. According to (1)

$$W_2 = W - (W_1 + W_3). \tag{4}$$

We can see from Fig. 3 that at low temperatures the main component of the rate of mass loss in synthetic graphite is the interstitial reaction. With rising temperature the mass losses result primarily from the crumbling of the unoxidized filler particles. The granulometric composition of the filler and the density of the graphite affect the magnitude of mass loss due to particle crumbling (Fig. 2) only insignificantly in comparison with the influence exerted by them on the graphite mass loss due to interstitial reaction. The share of interstitial reaction in the over-all loss of graphite mass for an identical granulometric composition of the filler is higher in the case of a graphite that is less dense, and it is higher for a graphite with a fine-grained filler in the case of equal density.

NOTATION

Here W is the total mass loss rate, kg/m^2 sec; W_1 is the chemical reaction rate, kg/m^2 sec; W_2 is the rate of reaction inside pores based on external surface area unit, kg/m^2 sec; W_3 is the increase of mass loss rate due to fall of nonoxidized particles of fill is an increase of actual reactive surface, kg/m^2 sec; τ is the oxidation time, sec; T is temperature, °K; R is the universal gas constant, cal/deg. mol.

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