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Oxidation of Carbon Powders by Steam

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Abstract: The oxidation kinetics of a diamond powder, P-803 carbon black, and the OSUNT raw material (obtained by electric arc synthesis of single-walled carbon nanotubes) in a stream of steam in the temperature range 600–1315 K was studied. The parameters of the kinetic equations were determined. The temperature dependence of the oxidation rate was found to consist of three regions with different activation energies.

Keywords: diamond powder, carbon black, single-walled carbon nanotubes, oxidation kinetics, steam.

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This paper presents the results of a study of the oxidation of various carbon powder materials (P-803 commercial carbon black, A30 dispersed diamond powder, and a material containing single-walled carbon nanotubes (OSUNT raw material)] in a stream of steam.

Oxidation of various types of carbon materials using oxygen, carbon dioxide, and steam as oxidizers has been studied for many years. The results of these studies are summarized in several reviews. One of the first was a paper [1] published in 1959. A detailed analysis of the published results is also presented in a monograph [2]. Research on the oxidation of carbon materials has continued in subsequent years. Closest to the present work is the study [3], which describes the oxidation of charcoal powder in a stream of air, steam, and CO_2. Use of steam as oxidizer allowed us to perform oxidation in a broader temperature range. The oxidation kinetics of various grades of graphite and charcoal by steam was studied in [4].

In most of our work, we used the material containing single-walled carbon nanotubes [5]. The OSUNT raw material was produced by electric arc synthesis using nickel–yttrium catalyst. This product contains 18–25% (wt.) single-walled carbon nanotubes, 20–30% (wt.) metal catalysts, and about 40–50% (wt.) amorphous carbon.

In addition, we performed further processing of previously obtained results for the oxidation of carbon black and diamond powder in a stream of steam [6].

The oxidation process was studied on a setup which has previously been used in similar studies [6]. The experiments were carried out under isothermal conditions in the temperature range 600–1300 K. The rate of oxidation at different degrees of conversion was determined from the mass change of the sample. The setup includes the following major components.

1. Automatic microbalance with magnetoelectric compensation of mass change with a sensitivity of 10^{-5} g [7].

2. Reactor, which was a vertically mounted tube of quartz glass 16.4 mm in inner diameter and 265 mm long. The central part of the tube 100 mm long was covered with a Nichrome electrical wire, which was insulated on the outside with asbestos and a metal casing. In the central part of the reactor is a region 20 mm long in which the temperature change along the length and cross-section does not exceed 5 K. Experiments can be conducted in the reactor at temperatures up to 1400 K. Since all of the investigated materials are powders, a material sample was placed in a quartz cup 9.3 mm in inner diameter and 4.1 mm in height. The heap formed during filling of the cup was removed with a razor blade. The sample mass was 7–9 mg. The cup was placed in

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a basket of Nichrome wire and suspend by a chain attached to the balance beam.

3. Chromel–Alumel thermocouple of 200 μm diameter wire, whose junction was 6–8 mm below the test specimen. The working temperature of the reactor was set using an VRT-2 high-precision temperature controller.

4. Electrically heated steam generator with a capacity of 4 g/h. The steam generator was located below the reactor. Steam filled the entire section of the tube and moved upward. The linear velocity of steam near the sample was 1.6 cm/s at a temperature of 600 K and 4.7 cm/s at a temperature of 1300 K. The vapor pressure near the sample was atmospheric. Since the top of the reactor was open, we checked the possibility of diffusion of air into the reaction zone. No diffusion was detected during operation of the generator.

5. Personal computer to record readings of the balance head and thermocouple. Thermocouple and balance readings were taken at intervals of 1 to 30 s.

Before the experiments, the OSUNT raw material sample was ground in a coffee grinder. The particle size in plan ranged from fractions of a millimeter to 1 mm. The specific surface of the OSUNT raw material sample was 200–300 m^2/g (Institute of Problems of Chemical Physics, Russian Academy of Sciences, E. I. Knerel'man and G. A. Davydova). The bulk density of the powder was about 0.0016 g/cm^3.

The P-803 carbon black powder consists of spherical particles with an average diameter $d_{10} = 0.26$ μm. The carbon black specific surface determined by krypton absorption at the liquid nitrogen temperature using the Brunauer–Emmett–Teller (BET) method was 7.9 m^2/g.

The diamond powder was explosively produced by detonation of an RDX based explosive. The diamond particles have a compact form with $d_{10} = 0.037$ μm, and their surface area determined by the same method as for carbon black was 44 m^2/g.

The first results of the experiments showed that the degree of conversion at which the oxidation rate of the OSUNT raw material sample is greatly reduced depends on temperature. At the lowest temperature in our experiments 604 K, only 36% of the initial mass of the sample was oxidized for 76 h, and the unoxidized residue accounted for 64%. Increasing the temperature to 750 K reduced the unoxidized residue to 23%, and with a further increase in temperature, it remained unchanged. In this temperature range, the unoxidized residue was black or dark-gray. This amount of the unoxidized residue approximately corresponds to the content of the nickel–yttrium catalyst in the nanotube raw material studied. At temperatures above 750 K, the residue was gray–green. In all the experiments, the time of oxidation was several times larger than the time required for the sample to reach a constant mass. Consequently, the samples contained about 77% reactive mass. It consisted of amorphous carbon (60%) and nanotubes (40%). The temperature dependence of the fraction of the unoxidized residue is shown in Fig. 1 (η is the degree of oxidation).

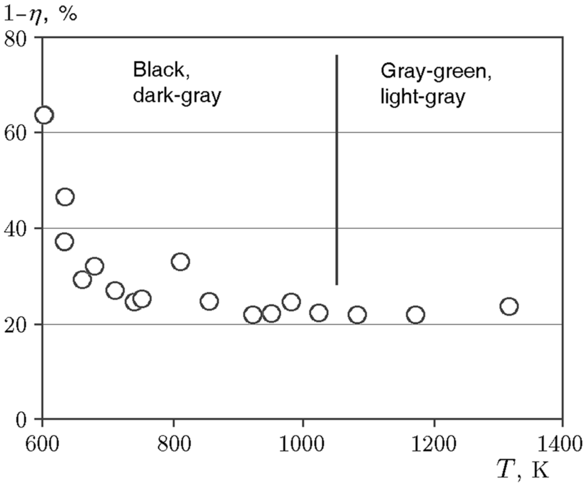

Fig. 1. Dependence of the fraction of the unoxidized residue of the OSUNT raw material sample versus temperature.

The results of a study [8] of carbon oxidation by steam have shown that the order of the reaction depends on the pressure of the oxidizer and temperature. At atmospheric pressure and a temperature of ≈1000 K, the reaction is of the first order. In our work, the steam pressure in all experiments was atmospheric.

Many authors who have studied carbon oxidation by steam came to the consensus [1, 2, 8] that the reaction proceeds according to the equation

$$C(s) + H_2O(g) = CO + H_2$$

[(s) refers to the solid state and (g) to the gaseous state]. Desorption of CO from the carbon surface is much faster than the desorption of hydrogen. Consequently, the oxidation kinetics of carbon by steam can be determined from the change in the sample mass during the experiment.

In studying oxidation, we assumed that the start and end of the process corresponded to 1 and 99% oxidized mass. This interval was taken as 100% oxidation of the sample. The dependence of the amount of the reacted material on time was plotted with a mass increment of 5%. The relative reaction rate was determined from the formula

$$W_i = \frac{m_{i-1} - m_{i+1}}{m_0(t_{i+1} - t_{i-1})}.$$

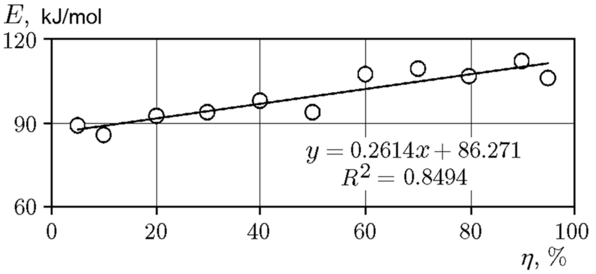

Fig. 2. Activation energy versus degree of oxidation of the OSUNT raw material in the temperature range 600–750 K.

Here m_0 is the initial mass, m_i is the mass of the sample in the ith step, t_i is the time of the experiment in the ith step. Oxidation rate constants at different degree of conversions were calculated. The oxidation rate for the degree of conversion η was determined as the average value in the region $\eta \pm 5\%$.

The dependence of the activation energy on the degree of oxidation in the temperature range 600–750 K is shown in Fig. 2. It is seen that with increasing degree of oxidation from 5 to 90%, the activation energy increases from 90 to 110 kJ/mol. However, the temperature dependence of the average rate of oxidation is well described by the Arrhenius law with an activation energy of 106 kJ/mol.

The temperature dependence of the oxidation rate is shown in Fig. 3 (change in the average rate of complete oxidation of the sample from 1 to 99% reacted mass). The dependence consists of three regions in the temperature ranges 600–750, 750–1100, and 1100–1350 K. A similar types of temperature dependence of the rate of oxidation has been observed previously for the oxidation of diamond powder and carbon black [6].

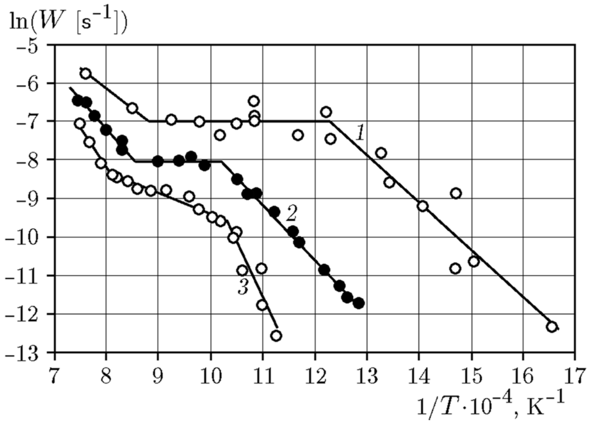

Fig. 3. Average rate of oxidation versus temperature: (*1*) OSUNT raw material; (*2*) carbon black; (*3*) diamond powder.

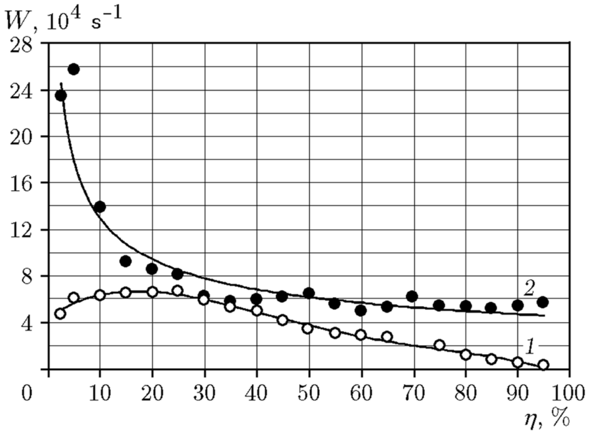

Fig. 4. Rate of oxidation of the OSUNT raw material versus degree of conversion at temperatures of 711 (*1*) and 982 K (*2*).

The dependence of the oxidation rate on the degree of conversion has differences in different temperature ranges. Figure 4 shows the change in the oxidation rate as a function of the degree of conversion at a temperature of 711 K. At the beginning of the process, the rate dramatically increases to a maximum which corresponds to 25% reacted mass. Subsequently, the rate of oxidation decreases gradually to zero at the end of the reaction. Similar behavior of the dependence is observed throughout the range 600–750 K. The position of the maximum rate corresponds on average to the oxidation of 10–20% of the sample mass.

In the range 750–1100 K, the oxidation rate is almost independent of temperature. The curve of the change in the oxidation rate versus degree of conversion also begins with a sharp rise. The maximum rate correspond to a degree of conversion of 10–20%. By the time of oxidation of 30% of the sample mass, the rate is reduced by a factor of 5–6. Then it further decreases on average by a factor of about two during the oxidation of 90% of the sample mass. As an example, Fig. 4 also shows the dependence of the oxidation rate on the reacted portion of the sample at a temperature of 982 K.

In the high-temperature region (1100–1350 K), we have only two experimental points. The activation energy cannot be reliably determined because of the small number of experiments and because of the large difference between the dependences of the oxidation rate on the degree of conversion at temperatures of 1175 and 1315 K. The resulting energy of 75 kJ/mol should be regarded as approximate.

The experimental results lead to the following suggestions about the nature of the oxidation reaction of the OSUNT raw material in different temperature ranges. In the low-temperature range (600–750 K), the reaction generally proceeds in the kinetic regime. After the oxidation process has become steady, the reaction occurs on the surface of all particles throughout the sample. Over time, the reacting surface decreases, which leads to a gradual reduction in the mass reaction rate.

At medium temperatures (750–1100 K), up to 30% of the sample mass is oxidized at a high rate in the initial region as a result of penetration of the oxidizer into the surface layer of the material. Subsequently, the reaction proceeds layer-by-layer in the diffusion regime. The gradual relatively small decrease in the mass rate is caused by the accumulation of the inert material in the reacting layer.

The higher average rate in the range 1100–1350 K as compared with that in the previous temperature region is caused by a sharp increase in the rate at a temperature of 1315 K. We have not been able to determine the cause of the increase in the rate of oxidation in the high-temperature region.

In addition to the data for the OSUNT raw material, Fig. 3 also presents the results of studies of the oxidation of carbon black and diamond powder by steam. In contrast to [6], we obtained dependences of the average oxidation rate of the entire sample (1 to 99% of the mass). It is seen that the nature of the temperature dependence is similar for all three materials.

In experiments with carbon black, the temperature regions are 750–950, 950–1200, and 1200–1335 K. These regions coincide within the error with those determined in [6]. In the low-temperature range (780–950 K), where the reaction proceeds in the kinetic regime, the activation energy It is equal to 121 kJ/mol, which is lower than the activation energy of 130.4 kJ/mol corresponding to the oxidation of 10% of the sample mass obtained in [6].

In experiments with the diamond powder, the temperature ranges were 800–1000, 1000–1250, and 1250–1335 K. As in the experiments with carbon black, they coincide with the ranges obtained in [6]. However, the activation energy of 124 kJ/mol in the low-temperature region (800–1000 K), determined from the average rate of oxidation of the entire sample, was found to be significantly lower than the value of 180.6 kJ/mol corresponding to the rate of oxidation at the beginning of the process. Thus, in both cases, at the initial stage of the process, the oxidation rate is more strongly temperature dependent than the average rate.

In the low-temperature region, the highest rate is observed for the OSUNT raw material. At a temperature of 800 K, it is about 30 times higher than the oxidation rate of carbon black and 35 times higher than the oxidation rate of diamond powder. The difference between the oxidation rates of carbon black and diamond powder is due to the difference in particle size between these materials. Particles of the OSUNT raw material are much larger than those of carbon black and diamond powder. Consequently, the higher rate of oxidation of the OSUNT raw material is due to the significantly higher reactivity of carbon nanotubes. This is also reflected in the fact that the transition to the diffusion regime of the reaction for the OSUNT raw material occurs at a lower temperature than for carbon black and diamond powder.

In the medium-temperature range, the rates differ by a factor of approximately three. All the investigated materials have a high-temperature region. The transition to this region occurs in the temperature range 1100–1250 K. As mentioned above, we have not been able to determine the cause of this increase in the rate of oxidation.

REFERENCES

1. P. L. Walker, P. Rusinko, and L. G. Austin, "Gas Reaction of Carbon," Adv. Catal. **XI**, 133–221 (1959).
2. E. S. Golovina, *High-Temperature Combustion and Gasification of Carbon* (Energoizdat, Moscow, 1983) [in Russian].
3. N. N. Volkova, E. A. Salganskii, A. A. Zhirnov, and G. B. Manelis, "Kinetic Laws of Carbon Oxidation by Air, Steam, and CO_2 with Filtration of the Gaseous Reactant," Khim. Fiz. **26** (2), 53–59 (2007).
4. E. I. Gusachenko and L. N. Stesik, "Carbon Oxidation by Vapor," Khim. Fiz. **27** (4), 14–20 (2008).
5. A. V. Krestinin, "Single-Walled Carbon Nanotubes: The Mechanism of Formation and the Prospects for the Production Technology Based on the Electric Arc Process," Ros. Khim. Zh. **48** (5), 21–27 (2004).
6. E. I. Gusachenko and L. N. Stesik, "Oxidation of Fine Powders of Diamond and Amorphous Carbon by Steam," Khim. Fiz. **30** (3), 31–37 (2011).
7. L. N. Gal'perin, Yu. E. Kolesov, and N. A. Zelenov, "Automatic Balance with a Magnetoelectric Mass Compensator," Izmer. Tekh., No. 4, 23–25 (1971).
8. G. Blyholder and H. Eyring, "Kinetics of the Steam-Carbon Reaction," J. Phys. Chem. **63** (5), 693–696 (1959).