THE CO_2-GRAPHITE REACTION AT 1200-2400°C

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Reaction-rate results are presented for CO_2 in the range 1200-2400°C interacting with graphite of grades VPP, MPG-8 (1), and pyrographite.

Graphite is a high-temperature constructional material, and its working capacity may be limited by interaction with gases such as H_2O, CO_2, O_2, NO, etc. In some cases one has to perform engineering calculations on the rate of interaction of graphite with corrosive gases, but for this purpose one needs to know the reactivity in relation to each gas. We have examined the rates of interaction of some grades of graphite with CO_2 over the range 1200-2400°C at partial pressures of CO_2 of $(0.08\text{-}0.34)\cdot 10^5$ N/m^2 and total pressures of Ar—CO_2 of $1\cdot 10^5$ N/m^2.

Published studies on the interaction of carbon with CO_2 give very little evidence that can be directly used in engineering calculations, the reasons being that tests at high temperatures do not occur in the purely kinetic region but in the transitional or diffusion region. One can avoid diffusion inhibition most completely by conducting experiments at low pressures, but then the results [1, 2] are difficult to use in calculations when the pressure is several atmospheres or more. In such cases one has to extrapolate the experimental results from the range 10^{-6}—10^{-5} atm to the range 10^{-1}—10 atm. Experiments have been reported [3, 4] for CO_2 pressures of $0.1\text{-}1.0\cdot 10^5$ N/m^2. The effects of diffusion were not completely eliminated, because the rate at which the gas was flowing was comparatively small (0.2-0.8 m/sec). In [5], experiments were done with gas flow speeds of 200-500 m/sec, and the gas flow was heated by an electric arc with a tungsten cathode. Unfortunately, the results from this study are unusable on account of effects from tungsten vapor. We have found that a tungsten cathode gives rise to tungsten vapor that then partially deposits on the graphite and distorts the reaction rate. This is why in [5] low maximum reaction rate of graphite with CO_2 was found in the range 1600-1800°C, although one is indicated by the results of [1-4, 6].

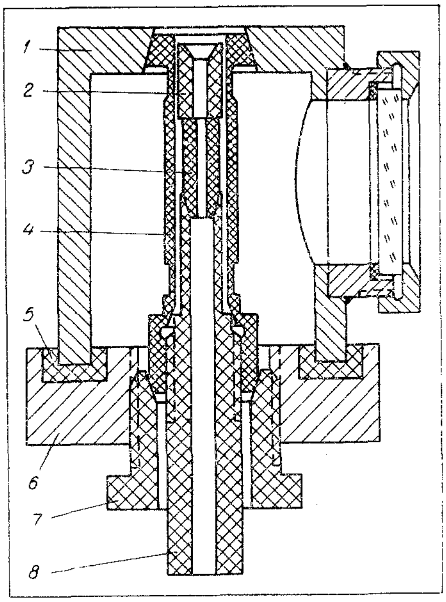

Fig. 1. Section of oven: 1) upper current lead; 2) input bushing; 3) graphite specimen; 4) graphite tubular heater; 5) insulator; 6) lower current lead; 7) outlet tube. The gas flows along the central channel from top to bottom.

The apparatus we used for the experiment consisted of an electric arc heater, a mixer, and an oven. The heater served to heat the argon. In the mixer, the hot argon was mixed with CO_2 at room temperature. This gave a mixture of specified composition and temperature. This passed to the oven (Fig. 1), where CO_2 reacted with the graphite specimen 3, which was a 30 mm cylinder with outside diameter 12 mm. The reaction occurred within the axial channel of diameter 3 mm. The flow rate for the gas mixture was designed such that the gas speed within the working channel was on average 200 m/sec. The temperature of the specimen was measured with an OPPIR-017 pyrometer. A mirror was used to sight the pyrometer through the outlet tube 8 on a hole of diameter 2.5 mm and length l = 15 mm in the lower end of the specimen. The specimen temperature

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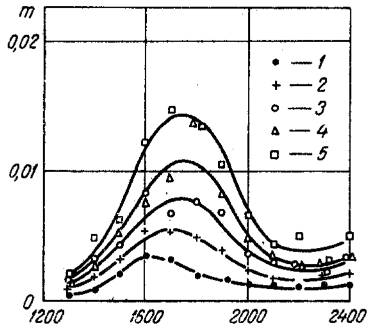

Fig. 2

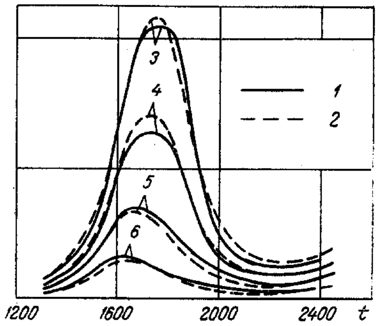

Fig. 3

Fig. 2. Reaction rate m (kg/m^2 · sec) for VPP graphite in CO_2 as a function of temperature t (°C). Gas pressure (Ar + CO_2) $9.8 \cdot 10^4$ N/m^2 (1 atm), flow speed w = 200 m/sec, CO_2 partial pressure N/m^2: 1) $0.81 \cdot 10^4$ 2) $1.51 \cdot 10^4$; 3) $2.1 \cdot 10^4$; 4) $2.61 \cdot 10^4$; 5) $3.46 \cdot 10^4$.

Fig. 3. Reaction rate m (kg/m^2 · sec) for VPP graphite in CO_2 as a function of temperature t (°C). With calculated allowance for diffusion: 1) from experiment; 2) from (12); CO_2 pressures (N/m^2) at surface of: 3) $1.81 \cdot 10^4$; 4) $1.35 \cdot 10^4$; 5) $0.9 \cdot 10^4$; 6) $0.45 \cdot 10^4$.

was controlled by the currents of the tubular graphite heater 4. When a set temperature has been reached, the argon flow was turned on and the arc was struck. The mixer was supplied with a set flow rate for CO_2, and the gas temperature was adjusted via the heater power (we omit the description of gas temperature monitoring). The loss in weight of the specimen during the experiment was determined by weighing with an ADB-200 balance. The running time was measured with a 51-SD clock. The reaction rate m in kg/m · sec) was estimated from the loss in weight of the specimen as a ratio to the surface of the working channel and to the running time. The carbon dioxide flow rate was measured before and after the experiment by an RS-3 rotameter. The argon flow rate was established from the supercritical pressure drop at the flow throttle. The calibrations for flow were performed by means of GSB-400 gas meters. The error in measuring the argon flow rate was ± 4%, while that for the carbon dioxide was ± 6%.

Although the gas flow speed was comparatively high (200 m/sec), the reaction rate depended not only on the kinetics of the C + CO_2 reaction but also on the gas mixing rate in the boundary layer, i.e., there was some diffusion retardation. The effects of this were seen in that the concentration of the CO_2 directly at the graphite surface C_s was less than that in the initial gas mixture C_g. To allow for diffusion by calculation we need to know the carbon dioxide concentration that realized directly at the surface C_s, and the reaction rate has to be referred to this concentration, not to C_g. To calculate C_s we used the method of [7], which is based on the empirical relationship

$$m = gB. \tag{1}$$

The analogy between heat and mass transfer [7] gives

$$g = \alpha / c_p. \tag{2}$$

To calculate α we used the empirical relationship for the inlet part of the tube with a laminar boundary layer (this was the case of a specimen) [8]. The concentration head B was obtained by using the law of conservation for C in the boundary layer [7]:

$$B = \frac{C_g - C_s}{\frac{\mu_{CO_2}}{\mu_C} + C_s}. \tag{3}$$

From (1) and (3) we get

$$C_s = \frac{C_g - \frac{m\mu_{CO_2}}{g\mu_C}}{1 + \frac{m}{g}}. \tag{4}$$

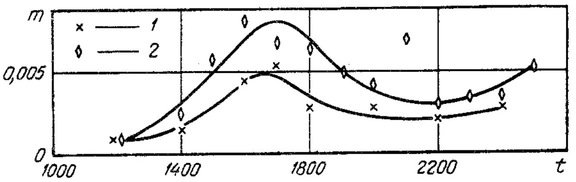

Fig. 4. Reaction rate m (kg/m • sec) as a function of temperature t (°C) (diffusion effects present) for: 1) pyrographite; 2) MPG-8 (1) graphite for a partial pressure of $2.1 \cdot 10^4$ N/m^2 of CO_2 in the initial flow and a speed of 200 m /sec.

From (4) we calculated the carbon dioxide concentration at the graphite surface in each experiment.

We used artifical polycrystalline graphites of grades VPP and MPB-8 (1), as well as pyrographite of grade UPB-1. The initial material for making the medium-grained VPP graphite (density 1.9-1.95 g/cm^3, graphitization temperature 2800°C) was fired oil coke (filler) and coal sinter (bonding agent). For the fine-grained MPG-8 (1) graphite (density 1.8 g/cm^3, graphitization temperature 2800°C), the filler was unfired coke. The pyrographite had a high degree of orientation in the crystallites, the layers of atoms in these lying parallel to the deposition surface. This was responsible for marked anisotropy in many properties of the pyrographite, including the reactivity in oxidation.

The reaction rate for the pyrographite (density 2.2 g/cm^3, production temperature 2100°C) was determined on the end face, i.e., on the surface intersecting the layers of atoms at a right angle.

Figure 2 shows the reaction rate for VPP as a function of temperature for 5 CO_2 concentrations in the initial gas mixture, $C_g = 9.1; 16.6; 23; 28.6;$ and 37.5 wt.%. These relationships are distorted by diffusion. From (4) we determined the corrections for diffusion. The solid line in Fig. 3 shows the true m = f(t) reaction rates (corrected for diffusion) for C_s of 5, 10, 15, and 20 wt.%, while Fig. 4 shows m = f(t) for C_g of 23 wt.% for MPG-8 (1) and pyrographite reacting on the end surface. These relationships were derived for only one CO_2 concentration, so we could not introduce corrections for diffusion. Each point on these curves is the mean of not less than 3 runs.

For convenience in using the results in engineering calculation, the experimental relationships (solid lines in Fig. 3) were approximated by an analytical expression (broken lines). The choice of the approximating expression was based on the following concept of the reaction mechanism. It was assumed [1, 9] that the reacting surface had active atoms (mass reaction rate m_a) and inactive ones (reaction rate m_n). The total reaction rate was

$$m = m_a + m_n. \tag{5}$$

The active atoms are evidently ones with unsatisfied valencies. The tests showed that the reaction rate of VPP in the range of partial pressures of CO_2 used was directly proportional to the carbon dioxide pressure, i.e., was directly proportional to the number of collisions of CO_2 with the graphite surface ν. We denote the fraction of the reacting surface occupied by active atoms by θ, in which case the nonactive atoms occupy $1-\theta$.

Then we get that

$$m = G\nu\,[\varphi_a\theta + \varphi_n(1-\theta)]. \tag{6}$$

We assume that the active atoms were transformed to nonactive ones at high temperatures, which may arise from increased thermal mobility, particularly for the active atoms, which are less firmly bound. The final result of motion in the active atoms is that they become incorporated into the hexagonal network in such a way as to be bound by free bonds.

Below 1500°C, the rate of conversion of active atoms to others is small, and the production of hole defects predominates, which are produced where a carbon atom reacts with CO_2. Therefore, at low temperatures the entire reacting surface should be coated only with active atoms and $\theta = 1$. Above 2200°C, the conversion rate is so large that the active atoms formed by C + CO_2 are transformed to nonactive ones before collision with CO_2 can occur. Therefore, one assumes that in this case $\theta = 0$. In the intermediate range 1500°C < t < 220°C, both species are present and $0 < \theta < 1$. The relationship between the two species in this temperature range is dependent on the temperature and the frequency of the collision of CO_2 molecules with the surface, i.e., from the partial pressure of CO_2.

The following is the proportion of the surface occupied by the active atoms as a function of temperature and partial pressure of CO_2 (approximating expression):

$$\theta = \frac{1}{1 + \exp[D(T - T_g)]} = \frac{1}{1 + \exp[0.014(T - T_g)]} \qquad (7)$$

The T_g of (7) is itself a function of the partial pressure p_p of CO_2:

$$T_g = (Ep_p)^{\frac{1}{31}}. \qquad (8)$$

When VPP reacts with CO_2, the constant E is $28.5 \cdot 10^{-5}\ \mathrm{deg}^{31} \cdot \mathrm{m}^2/\mathrm{N}$. The temperature factors φ_a and φ_n are approximated as

$$\varphi_a = \exp\left(-\frac{B_1}{T}\right) = \exp\left(-\frac{27000}{T}\right), \qquad (9)$$

$$\varphi_n = CT^7 = 1.42 \cdot 10^{-31} T^7. \qquad (10)$$

The laws from the molecular kinetic theory of gases [10] imply that the collisional frequency ν for CO_2 molecules with unit surface is dependent on the pressure and temperature:

$$\nu = F \frac{p_p}{\sqrt{T}}. \qquad (11)$$

Substitution of (7), (9), (10), and (11) into (6) gives a final expression for approximating the experimental results:

$$m = A \frac{p_p}{\sqrt{T}} \left[\frac{\exp\left(-\frac{B_1}{T}\right)}{1 + \exp[D(T - T_g)]} + CT^7 \left(1 - \frac{1}{1 + \exp[D(T - T_g)]}\right) \right]. \qquad (12)$$

When VPP reacts with CO_2, the constant A is $65.6\ \mathrm{kg} \cdot \mathrm{deg}^{1/2}/\mathrm{sec} \cdot \mathrm{N}$. Expression (12) can be recommended for use in engineering calculations for VPP reacting with CO_2 over the range 1200-2600°C at partial pressures of CO_2 of $(0.05\text{-}0.2) \cdot 10^5\ \mathrm{N/m}^2$.

NOTATION

m_a, m_n	are the rates of reaction of more and less active carbon atoms, $\mathrm{kg/m^2 \cdot sec}$;
C_g, C_s	are the weight fractions of carbon dioxide in the initial gas mixture and at graphite surface;
g	is the mixing rate in the boundary layer, $\mathrm{kg/m^2 \cdot sec}$;
B	is the concentration head;
α	is the heat transfer coefficient, $\mathrm{W/m^2 \cdot deg}$;
c_p	is the heat capacity, J/kg·deg;
μ_{CO_2}, μ_C	are the relative molecular and atomic masses of carbon dioxide and carbon;
f	is the functional relationship;
T, t	are temperatures in °K and °C respectively;
θ	is the fraction of the surface occupied by active C atoms;
ν	is the frequency of CO_2 collisions per unit area, $\mathrm{1/m^2 \cdot sec}$;
p_p	is the partial pressure of carbon dioxide at graphite surface, $\mathrm{N/m^2}$;
φ_a, φ_n	are factors expressing dependence of reaction rate on temperature for active and inactive C atoms respectively;
A, B_1, C, D, E, F	are constants.

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