REGULARITIES OF THE HIGH-TEMPERATURE REACTION OF CARBON

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REGULARITIES OF THE HIGH-TEMPERATURE REACTION OF CARBON

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It was shown ($^{1-3}$) that, in the interaction of carbon with a gaseous reagent (CO_2 and O_2) in the high-temperature region above 2300° K, when the conditions of the so-called developed diffusion regime of the reaction are realized and the possibility of diffusion penetration of the gas phase into the reacting specimen is excluded, a change in the density of the solid is observed. It was suggested that the change in density is explained by the removal of carbon from the volume of the solid to the surface on which the reaction takes place, owing to a considerable increase in the diffusion of carbon atoms. In order to study this peculiar new regime of "internal" reaction at high temperatures and its basic regularities, an experimental investigation was carried out in which the distribution of carbon density over the volume of a carbon specimen reacting in carbon dioxide was determined as a function of time at different temperatures.

The work was carried out, as before ($^{1-3}$), with spherical carbon particles 15 mm in diameter, made from graphitized carbon of grade VGM-4 at the Kudinovo plant. The experimental procedure was essentially the same as previously (^{4}). Heating of the carbon particle was carried out in the inductor of a high-frequency generator. In order to record the change in the specimen diameter with time, the particle was photographed in two projections—front and side. Processing of the film and measurement of the particle dimensions were performed on an IT tool microscope, which makes it possible to measure the diameter with an accuracy of ±0.005 mm.

The depth of loosening of the carbon and the distribution of the density γ of carbon along the radius of the specimen were estimated by successively removing carbon layers 0.2–0.25 mm thick from the specimen and determining the density of the removed layer. For this purpose, the spherical particles were successively ground down with the aid of metal diaphragms whose diameters differed by 0.5 mm. The layers were removed until the density of the core of the particle became equal to the initial density. All data were obtained for the interaction of carbon with carbon dioxide. The relative concentration of carbon dioxide with nitrogen as diluent was 50%; the flow velocity was 0.6 m/sec.

Fig. 1

Figure 1: Fig. 1

We note that, for a comparative assessment of the nature of the density change, it proved more convenient to use not time but the degree of carbon removal (gasification) from the specimen.

Figure 1 gives the picture of the distribution of carbon density along the radius of a spherical particle and its transformation when the reaction temperature changes from 2300 to 3000° K (A) and when the removal time or degree of removal changes from 18 to 29% at $T = 2770°$ K (B). Similar experimental material was obtained for different degrees of carbon removal at various temperatures.

It is clear from the figures that, as the temperature rises and the reaction time increases, carbon is removed from ever deeper layers.

sample. The process is substantially nonstationary. The picture presented in Fig. 1 is very characteristic of the distribution of a diffusing substance in various solids (^{5}). It should be noted that the value of the relative surface density γ_S for a wide range of temperatures and degrees of burn-off of 15-30% changes only slightly, fluctuating around the value 0.5. The character of the density distribution in carbon specimens for different temperatures and burn-off times, presented in Fig. 1, is identical to the known picture of the concentration distribution in nonstationary diffusion from a semi-infinite space (^{6,7}). Moreover, this case of diffusion is characterized by constancy of the concentration at the boundary and by its being equal to one half of the initial concentration throughout the entire diffusion time.

Fig. 1. Distribution of the relative density of carbon along the radius of a spherical particle: **A**—for different temperatures at the same degree of carbon burn-off, 18.5% (*a*—2280°K; *b*—2770°K; *v*—2890°K; *g*—2970°K); **B**—for the same temperature of 2770°K and for different degrees of burn-off (*d*—18.5%; *e*—25.0%; *zh*—29.0%)

Bearing in mind the experimental fact that the depth of loosening is small in comparison with the particle radius, we can analyze the data from the standpoint of nonstationary diffusion from a semi-bounded space under the following boundary conditions:

for $t = 0$ and $-\infty < x < 0$, $\gamma = \gamma_0$;

for all $t > 0$ and $x = 0$, $\gamma = \gamma_S = \gamma_0/2$,

where γ_0 is the initial density of the specimen; γ_S is the density at the surface.

For such conditions, the solution of Fick' s second equation for one-dimensional nonstationary diffusion,

$$\partial\gamma/\partial t = D_c \partial^2\gamma/\partial x^2,$$

when the diffusion coefficient does not depend on concentration, is expressed through the known Gaussian error integral (^{8}), i.e.

$$\gamma = \frac{\gamma_0}{2}\left\{1 + \Phi\left(\frac{x}{2\sqrt{D_c t}}\right)\right\}, \qquad \text{where } \Phi\left(\frac{x}{2\sqrt{D_c t}}\right) = \frac{2}{\sqrt{\pi}}\int_0^{x/2\sqrt{D_c t}} e^{-\xi^2}\,d\xi. \tag{1}$$

In our case $x = R - r$; D_c is the coefficient of self-diffusion of carbon; t is the diffusion time; R is the particle radius. The integral for the Gaussian error-distribution function is readily calculated from tables (see (^{8})).

Using relation (1), from the values of γ/γ_0 obtained experimentally, the coefficient of self-diffusion of carbon is easily calculated. Estimation of the diffusion coefficient for the nonstationary conditions of our problem is admissible when, after a sufficient time has elapsed from the beginning of the process, a regular regime is established (^{9}). A distinctive feature of the regular regime is a linear relationship between the logarithm of concentration and time. It follows from the experimental data obtained by us that such a regular regime for a temperature of 2800°K is established when burn-off exceeds 15%, which corresponds to a time of more than 150 sec from the beginning of the process. At the same times, constancy of γ_S is reached and $\gamma_S/\gamma_0 = 0.5$. For higher temperatures, when the process proceeds more intensively, the regular regime will be established more rapidly, as is evidenced, in particular, by the fact that for these temperatures $\gamma_S/\gamma_0 = 0.5$ already at 8-10% burn-off.

The values of the coefficient of self-diffusion of carbon D_c, calculated from relation (1), are presented in Table 1 and in Fig. 2 in the coordinate system $\lg(D \cdot 10^5)$–$10^3/T$.

T, °K	2770	2770	2780	2890	2970	3070	3070	3200	3230
$D_c \cdot 10^5$, cm^2/sec	0.69	0.62	2.01	2.24	4.23	1.19	4.54	6.78	8.00

The linear dependence of $\lg(D_c \cdot 10^5)$ on $10^3/T$ indicates that the coefficient of self-diffusion of carbon is related to T by the relation

$$D_c = D_{c0}e^{-E/RT}.$$

According to the data of Fig. 2, $E = 75\,000$ cal/mol, and $D_{c0} = 1 \cdot 10^2$. Feldman $^{(10)}$ studied the self-diffusion of carbon in the temperature range 2100–2600°K,

Fig. 2. Dependence of the logarithm of the self-diffusion coefficient on $10^3/T$

Fig. 3. Change in relative density with change in the criterion $(R-r)/2\sqrt{D_c t}$. *a*–2770°K; *b*–2780°K; *v*–2890°K; *g*–2970°K; *d*–3070°K; *e*–3200°K; *zh*–3280°K

using the tracer-atom method, and obtained $E = 75\,400$ cal/mol. The theoretical analysis of the process carried out by Feldman establishes that this value of E corresponds to the mechanism of carbon self-diffusion along grain boundaries. It must unfortunately be noted that it is impossible to estimate the diffusion coefficient from Feldman' s data, since the value of the pre-exponential factor was not determined in the work.

The experimental results presented by us, their analysis, and the obtained relation for the self-diffusion coefficient apparently give a value for D_c suitable for approximate calculations. Further work in this direction will make it possible to refine this value.

In Fig. 3 the experimental data are presented as a function of the criterion $z = (R-r)/2\sqrt{D_c t}$. The experimental points for γ/γ_0, corresponding to different temperatures and radii, group around a single curve. From this it is evident that for $T > 2700$°K, when the process of diffusion of carbon atoms proceeds rather intensively, the concentration distributions of the solid phase are satisfactorily described by relation (1).

In conclusion it should be noted that the presence of an internal diffusion process of transfer of the solid substance itself during its reaction in a chemically active gaseous medium, due to the existence and formation through chemical interaction of defects at the solid body—gas interface, compels a reconsideration of the existing point of view on the behavior of a reacting solid body and, in the general case, in the analytical consideration of the problem, requires taking into account the behavior not only of the gas phase but also of the substance of the solid body.

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