Oxidation of Poco AXF-Q1 Graphite in Air

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Results of an experimental program to determine the reaction rate constant and reaction order of a fine grain graphite POCO AXF-Q1[†] are presented. The reaction rate constant is determined to satisfy an Arrhenius type equation for which the activation energy is 35,431 cal/mole and the effective collision frequency is 11,170 lb/ft^2-sec-atm$^{0.7}$. The reaction order is determined to be 0.7. The oxidation reaction equation which satisfies the test data is solved simultaneously with the oxidation diffusion rate equation to obtain oxidation rates as a function of surface temperature, pressure and convective film coefficient. Solutions were obtained assuming the products of oxidation are either carbon monoxide or a mixture of carbon monoxide and carbon dioxide. Oxidation rates plotted as a function of temperature tend to have a plateau in the 2500–3500°R temperature range before approaching the conventional diffusion limited value. If a plateau is indeed realized, the oxidation rate is approaching a diffusion limited value with carbon dioxide being the predominant product of oxidation. At higher temperatures, carbon monoxide becomes the predominant product, resulting in an increased oxidation rate which asymptotically approaches the conventional diffusion limited value. A comparison is made between experimental data and the results of this study. The implications of this comparison are 1) carbon monoxide is the primary product of oxidation at moderate and high wall temperature; 2) chemical equilibrium is not always realized at the oxidizing wall.

Nomenclature

A = effective collision frequency
B' = mass addition parameter [see Eq. (4)]
C_H = convective film coefficient
E = activation energy
k = reaction rate constant
K_i = mass fraction of specie i
$\tilde{K}_O$ = mass fraction of the chemical element oxygen
K_p = equilibrium constant
Le = Lewis-Semenov number
$\dot{m}_w$ = mass flux rate at wall
n = order of reaction
P = pressure
Pr = Prandtl number
R = universal gas constant
Sc = Schmidt number
T = temperature
u = component of velocity parallel to wall
v = component of velocity perpendicular to wall
X_{O_2} = mole fraction of oxygen
ρ = density

Subscripts

CO = carbon monoxide
CO_2 = carbon dioxide
D = diffusion
DL = diffusion limited
e = edge of boundary layer
O_2 = molecular oxygen
R = reaction rate
w = wall

Introduction

THE oxidation of graphite is normally insignificant below a temperature of approximately 900°F (Ref. 1). Above this threshold level, however, the oxidation process follows a rate law which may be written as follows[2]:

$$\dot{m}_{wR} = k(P_{O_2})_w^{\,n} \tag{1}$$

where $(P_{O_2})_w$ is the partial pressure of oxygen at the graphite wall; n is the order of the reaction; and k is the specific reaction rate constant.

Equation (1) should be applicable for all temperatures above the threshold level. Several problems, however, become apparent upon further examination. The first problem encountered is that of determining the reaction rate and the reaction order for the graphite of interest, since a large variation in these properties exists among the various graphites. These data can only be obtained through test. A survey of reaction rate data for graphites made in Ref. 2 suggests the reaction order may vary between 0 and 1.0.

The reaction rate constant is usually expressed in standard Arrhenius form as follows[2]:

$$k = Ae^{-E/RT_w} \tag{2}$$

where A is the effective collision frequency; E is the activation energy; R is the universal gas constant; and T_w is the wall temperature.

If the reaction order is assumed to be 0.5, then Ref. 2 suggests the following sets of reaction data to be representative of fast and slow reaction rates: 1) Fast reaction: $E = 44.0$ K cal/mole, $A = 6.729 \times 10^8$ lb/ft^2-sec-atm$^{1/2}$; 2) Slow reaction: $E = 42.3$ K cal/mole, $A = 4.473 \times 10^4$ lb/ft^2-sec-atm$^{1/2}$.

The second problem encountered in using Eq. (1) exclusively is to evaluate $(P_{O_2})_w$. This problem is inherent in the oxidation process since oxygen consumed at the wall must be continuously supplied by diffusion across the boundary layer. The diffusion of oxygen, in turn, requires that a gradient of oxygen exist across the boundary layer. It is apparent that the oxidation process must be "coupled" to the diffusion process. The simultaneous solution of the reaction rate equation with the diffusion rate equation is therefore required to solve for the two unknowns, $\dot{m}_{wR}$ and $(P_{O_2})_w$. It should be noted that $(P_{O_2})_w$, and consequently the mass fraction of oxygen at the wall, will never be zero; therefore, oxidation will never be diffusion limited although this limit may be very closely approached.

A third problem encountered in the oxidation analysis is to determine the products of oxidation. This information is required to compute the energy balance as well as the oxidation rate at the wall. Several sources of experimental data, e.g., Refs. 3 and 4, show that both CO and CO_2 are formed during the oxidation process, with CO_2 being the predominant product at low temperatures. Since oxygen must also be present, this study assumes CO, CO_2, and O_2 are in chemical equilibrium at the wall. Molecular nitrogen is also at the wall, but it is assumed to be chemically inert. Air consisting of N_2 and O_2 is assumed for the freestream.

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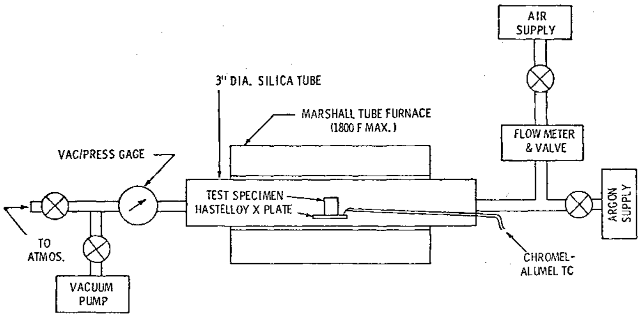

Fig. 1 Schematic of test equipment.

In addition to the CO–CO$_2$ product analysis, a secondary analysis was made in which it was assumed that CO was the only product of oxidation. It will be shown by a comparison of the two sets of results that the choice of oxidation products influences the predicted oxidation rate significantly.

Reaction Rate Tests

Oxidation tests were conducted at Teledyne Isotopes Energy Systems Division in Timonium, Md. as part of the SNAP 19 Pioneer program‡ to determine the reaction rate constant and reaction order of POCO AXF-Q1 graphite specimens. This grade of graphite is characterized by its high purity, high density and fine grain.

Oxidation of the ½ in. × ½ in. × 1 in. long specimens took place in a 3 in. diam silica tube. The specimen temperature was raised to the desired temperature level in an inert (argon) atmosphere. The inert gas was removed from the test chamber when the test temperature was attained and a slow moving stream of air was then passed through the tube. After a predetermined period of time the air flow was stopped, residual air was pumped from the test chamber, the chamber was backfilled with argon and the specimen was allowed to cool to room temperature. The chamber pressure was either 0.1 or 1.0 atmosphere and the specimen temperature was held constant within the range of 1200 to 1700°F for each of the twelve runs made. Figure 1 shows a schematic diagram of the test equipment.

Test Results

Results of the oxidation tests are summarized in Table 1. Exposed surface areas of each specimen were measured before and after test. It was assumed that no oxidation occurred on the bottom surfaces of the specimens. Oxidation rates were computed based on average exposed surface areas, exposure times and mass losses. Oxidation rates appear in the last column of Table 1.

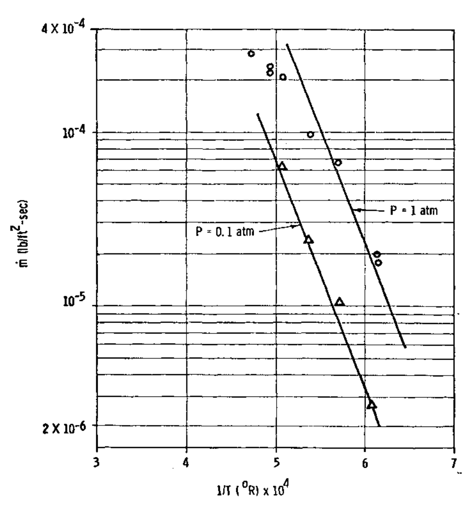

Fig. 2 Mass flux rate vs reciprocal of temperature.

Test data and the corresponding linear fit to the data are shown in Fig. 2. The poorer fit at the high oxidation rate levels is assumed to indicate that the partial pressure of oxygen at the graphite wall has dropped appreciably below the free-steam level. This deviation should be expected, of course, at the higher oxidation rates. The distance between the two curves dictates a reaction order of 0.7 and the simultaneous solution of the reaction rate equation for any two points on either curve dictates the following reaction rate constant factors: $E = 35{,}431$ cal/mole, and $A = 11{,}170$ lb/ft^2-sec-atm$^{0.7}$. These constants show POCO AXF-Q1 graphite is representative of a slow burning graphite.

Diffusion Equations

Lees[5] developed the following relationship between heat and mass transfer in a laminar boundary layer when $Le = Pr = Sc = 1$:

$$\tilde{K}_{O_e}/\tilde{K}_{O_w} = B' + 1 \tag{3}$$

where $\tilde{K}_{O_e}$ is the mass fraction of the chemical element at the edge of the boundary layer (0.2314); $\tilde{K}_{O_w}$ is the mass fraction of the chemical element oxygen at the wall; and B' is a parameter defined by the following equation:

$$B' = (\rho v)_w/\rho_e u_e C_H = \dot{m}_{w_D}/\rho_e u_e C_H \tag{4}$$

Table 1 Summary of results

Run no.	Temperature, °F	Test time, min	Pressure, atm	Avg exposed surface area, in.^{2}	Mass loss, g	Mass flux rate, lb/ft^2-sec
1	1200	60	0.1	2.2392	0.0665	0.2619×10^{-5}
2	1200	60	1.0	2.2473	0.4504	1.7674×10^{-5}
3	1200	60	1.0	2.2492	0.4994	1.9580×10^{-5}
4	1300	60	0.1	2.2478	0.2592	1.0169×10^{-5}
5	1300	60	1.0	2.1869	1.5950	6.4317×10^{-5}
6	1400	30	0.1	2.2413	0.3044	2.3953×10^{-5}
7	1400	30	1.0	2.1928	1.2171	9.7893×10^{-5}
8	1500	30	0.1	2.1891	0.7891	6.3576×10^{-5}
9	1500	30	1.0	2.0587	2.4497	20.9867×10^{-5}
10	1600	10	1.0	2.1784	0.9700	23.5602×10^{-5}
11	1600	10	1.0	2.1862	0.9961	24.1079×10^{-5}
12	1700	20	1.0	2.0900	2.2651	28.6719×10^{-5}

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where $(\rho v)_w$ is the convective mass flux rate at the wall. It is equal to $\dot{m}_{w_D}$, the graphite mass flux rate dictated by the diffusion of oxygen to the wall.

The mass loss rate due to diffusion can now be computed by combining Eqs. (3) and (4)

$$\dot{m}_{w_D} = \rho_e u_e C_H \left[\frac{0.2314}{K_{O_2} + \frac{16}{28} K_{CO} + \frac{32}{44} K_{CO_2}} - 1 \right]_w \tag{5}$$

In the special case of diffusion limited oxidation, the O_2 and CO_2 will disappear at the wall. Equation (5) then becomes the following:

$$\dot{m}_{w_{DL}} = 0.1734\, \rho_e u_e C_H \tag{5a}$$

Computational Method

Oxidation rates were computed for selected values of oxygen mole fraction (X_{O_2}) and temperature at the wall. The computations assumed CO and O_2 to be in chemical equilibrium with CO_2 in accordance with the following equilibrium constant[6]:

$$\mathrm{Log}_{10} K_p = 4.22 - [25{,}500/T(°\mathrm{R})] \tag{6}$$

Computations were carried out using the Thermal Analyzer Program (TAP-3) for ten preselected values of X_{O_2} ranging from 0.0001 to 0.2. Ultimately, Eqs. (1) and (5) were solved as a function of wall temperature (1600–5000°R range) for pressure levels of 0.1, 1.0, and 10 atm. Computed mass flux rates were normalized for simplicity of presentation. Normalized reaction and diffusion rates for constant X_{O_2} values were then plotted as a function of temperature. Intersections of corresponding pairs of these curves therefore define the oxidation rate that satisfies both Eqs. (1) and (5).

The convective film coefficient was treated as a parameter. It was reduced to 0.1 and 0.01 of its original value and the same method was used to obtain the simultaneous solution of the reaction and diffusion rate equations. A similar set of computations was carried out assuming the oxidation product to be CO only.

Results

Plots of oxidation rates as a function of temperature are shown in Figs. 3–5 for pressure levels of 0.1, 1.0, and 10 atm, respectively. These rates are normalized with respect to the diffusion limited rate computed by Eq. (5a). It is seen that the curves are characterized by a plateau at approximately 50% of the conventional diffusion limited value. The plateau is indicative of the oxidation rate approaching a diffusion limited value with CO_2 being the predominant product of oxidation. The plateau becomes less pronounced at low pressures and high convective film coefficients.

A comparison between the CO–CO_2 product solution and a solution that assumes only CO to be the oxidation product is shown in Fig. 6. As might be expected, the CO product assumption yields substantially higher oxidation rates in the moderate temperature range. In the lower temperature range the rates are almost equal because of the negligible influence of diffusion. In the high temperature range the rates converge because the product mixture is predominantly CO.

It is noted that the parameter $\rho_e u_e C_H$ is dependent on pressure and nose radius or some shape factor. Selecting a characteristic body dimension and pressure therefore fixes $\dot{m}_{w_{DL}}$.

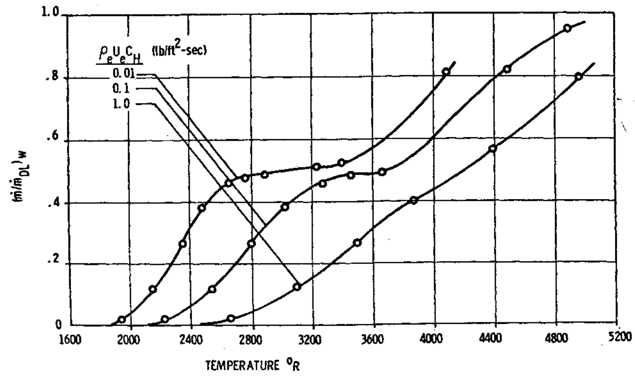

Fig. 3 Normalized oxidation rate—POCO AXF-Q1 graphite; $Le = Pr = Sc = 1.0$; $P = 0.1$ atm; products of oxidation = CO and CO_2.

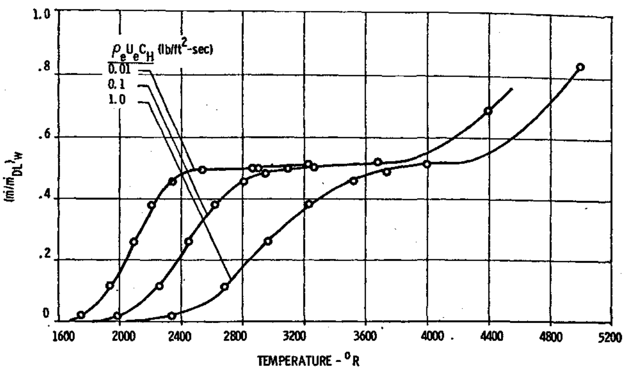

Fig. 4 Normalized oxidation rate—POCO AXF-Q1 graphite; $Le = Pr = Sc = 1.0$; $P = 1.0$ atm; products of oxidation = CO and CO_2.

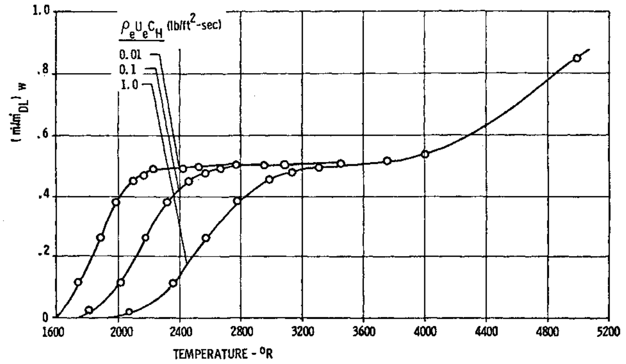

Fig. 5 Normalized oxidation rate—POCO AXF-Q1 graphite; $Le = Pr = Sc = 1.0$; $P = 10.0$ atm; products of oxidation = CO and CO_2.

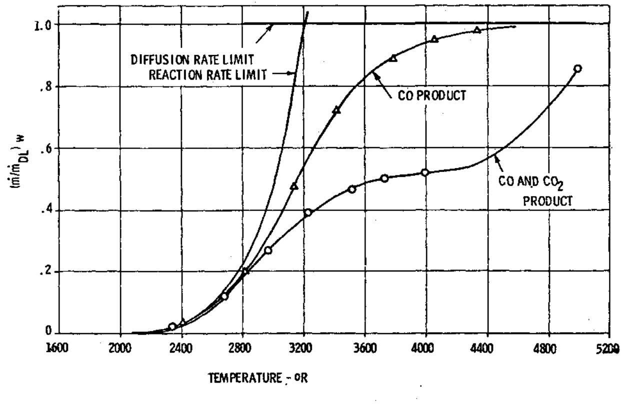

Fig. 6 Comparison of normalized oxidation rates; $P = 1.0$ atm; $Le = Pr = Sc = 1$; $\rho_e u_e C_H = 1$ lb/ft²-sec.

Discussion

The general trend of oxidation rate with temperature predicted in this study has been predicted previously in Ref. 7 and Ref. 8, which also postulated the formation of CO and CO_2 in chemical equilibrium with O_2.

A review of experimental results does not conclusively support nor refute the CO–CO_2 product results of this study. For example, Ref. 9 results support the CO product results as presented in Fig. 6. On the other hand, Ref. 7 presents some subsonic air jet data that support the CO–CO_2 product and also refers to another paper (Ref. 10) that does likewise. Reference 11 compares diffusion limited theory with test data. In this comparison the theory consistently predicted more oxidation than obtained in test. In general, measured recession was 75% of theory. It appears plausible that this difference was caused by the production of a large percentage of CO_2 in the oxidation product.

It is interesting to note that the oxidation plateau is not realized at low pressures and film coefficients as illustrated in Fig. 3. Under these conditions, oxidation does not approach a diffusion limited value until the wall temperature is well above 3000°R. A large quantity of low pressure experimental data is presented in Ref. 12 which also does not appear to approach a diffusion limited value at wall temperatures of about 3000°R. As noted in Ref. 12, these data are inconsistent with the generally accepted opinion that oxidation will be diffusion limited if the wall temperature is about 3000°R. The CO–CO_2 results of this study are in general agreement with the low pressure data presented in Ref. 12 and contrary to the generally accepted opinion just stated.

While the referenced experimental oxidation rates previously cited were for graphites other than POCO AXF-Q1, it is expected that these graphites oxidize in a manner similar to that of the POCO. When these rates are compared with the oxidation rate curves of Fig. 6, it is apparent that referenced experimental rates, in general, lie within the bounds of the CO and CO–CO_2 product curves. The implications of this comparison are the following: 1) carbon monoxide is the primary product of graphite oxidation at moderate and high wall temperatures; 2) chemical equilibrium between CO, CO_2 and O_2 is not always realized near the oxidizing graphite wall because the residence time of the CO product in this region is small when compared with the chemical relaxation time to approach equilibrium. In the extreme case of frozen flow, CO is the only oxidation product.

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