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Penetration depth and transient oxidation of graphite by oxygen and water vapor

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ABSTRACT

Equations are derived for the approach to equilibrium in the oxidation of graphite under assumptions of constant graphite density and linearized oxidation kinetics. A two-factor expression is assumed for the effective diffusivity. Equilibration may be estimated by observing the convergence of profiles with time or by means of an algebraic approximation. At large times, the profiles converge to the steady state. Oxidation depths show fair agreement with published measurements and follow closely the observed temperature trend.

1. Introduction

There is a fairly wide-spread interest in graphite oxidation due to its application as a structural material and moderator in gas-cooled reactors. The interest is motivated both by the need to evaluate effects of slow, long-term oxidation during normal operation from unavoidable coolant impurities, and by extremely rare possibilities of large-scale ingress of air or moisture. Many aspects of this problem have been under study for perhaps 50 years.

This letter proposes an analytical procedure, which though burdened with several restrictive assumptions, may find some interesting application. Equations for transient oxidation profiles are derived for a semi-infinite slab based on the assumptions of constant graphite density and linearized oxidation kinetics. The solution also assumes that oxidant transport may be described by a Fickian effective diffusivity. An expression for it is adopted based on data in published reports. Perhaps of greater interest is the observation that the transient profiles converge to the time-steady shape at large times, thereby yielding information on the equilibrium[1] penetration depth of oxidation.

2. Transient oxidation distribution equation

A general expression for oxidant transport in a semi-infinite slab may be written:

$$\frac{\partial(\varepsilon u)}{\partial t} = \frac{1}{\partial x} D_{eff}\left(\frac{\partial u}{\partial x}\right) - R_1 \rho N_u \tag{1}$$

The symbol u is the concentration of oxidant (mol/m^3-void), ε is the local void fraction, R_1 is the local oxidation rate calculated as (mol C oxidized) (mol C)$^{-1}$ s^{-1}, ρ is the local molar density of graphite (mol C/m^3), and N_u is a stoichiometric constant (mol oxidant utilized per mol C oxidized). Units of each term are mol O_2 (or H_2O) per m^3-graphite per second. The equation assumes that transport of O_2 or H_2O in graphite follows a Fickian format with a semi-empirical diffusivity, D_{eff}.

Graphite density appears explicitly as ε and ρ, and implicitly in the functional dependence of D_{eff} and R_1 on density. Hence Eq. (1) cannot be solved without additional information and then only simultaneously with the general oxidation equation:

$$\frac{\partial \rho}{\partial t} = -R_1 \rho \tag{2}$$

Under some restrictive assumptions, (1) may be solved independently of (2). If the density is assumed constant, and if D_{eff} is assumed to depend solely on the density, then (1) may be written,

$$\frac{\partial u}{\partial t} = \frac{D_{eff}}{\varepsilon}\frac{\partial^2 u}{\partial x^2} - R_1 \rho N_u/\varepsilon \tag{3}$$

Further, a linearized kinetics expression must be assumed for R_1.

$$R_1 = K_1 P_u \tag{4}$$

where K_1 has an Arrhenius temperature dependence, and P_u is the partial pressure of O_2 (or H_2O) in the void space at (x, t). The linearization introduced by Eq. (4) preserves the trend of R_1 with temperature and oxidant pressure compared with the full non-linear expressions, and permits an analytical solution to (3). Since $P_u(x, t)$ equals $RT_u(x, t)$, Eq. (3) can be written,

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[1] The term *equilibrium* is used here in the intuitive sense, and is not precisely defined. It is understood that as the profiles approach some final shape, they continue to progress inward as the oxidation progresses. If the inward movement is relatively slow, we may more properly call the situation *quasi-steady*.

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$$\frac{\partial u}{\partial t} = \frac{D_{eff}}{\varepsilon}\frac{\partial^2 u}{\partial x^2} - \frac{A}{\varepsilon}u \tag{5}$$

where

$$A = K_1 RT\rho N_u \tag{6}$$

Constant density is assumed out of necessity to obtain a relatively simple analytical solution. However, the result nevertheless has some utility by illustrating approximate penetration depths, equilibrium times and trends with temperature. Perhaps somewhat surprising, realistic oxidation depths are obtained, at least for the case shown below, where experimental and calculated penetration depths are compared.

3. Steady state

The solution of (5) must trend toward the steady state at large t. At quasi-steady state, (5) becomes

$$0 = u'' - B^2 u \tag{7}$$

where

$$B^2 = A/D_{eff} \tag{8}$$

The double prime signifies the second derivative with respect to x. The solution of (7) is readily obtained for a semi-infinite slab with the boundary conditions

BC1: $u(x = 0) = U$ (a constant).
BC2: $u(x \to \infty) = 0$.

The steady state solution is,

$$\frac{u(x)}{U} = \exp(-Bx) \tag{9}$$

This is a slight variation of the Thiele equation with B replacing $\surd(K_1/D_{eff})$. The effect of this modification is that the surface oxidation rate, obtained by integration of (9) from $x = 0 \to \infty$ approaches the accepted $\surd T$ dependence only at high temperature. This is due to the additional temperature dependences in the definition of the material parameter, B. Moreover, consideration of the surface boundary condition, i.e., alteration of U due to a limited convective driving force, may cause further departure from the idealized $\surd T$ dependence of the surface oxidation rate (see further in [1]).

4. Transient solution

Assume the following boundary conditions for a semi-infinite slab exposed to oxidant at the $x = 0$ surface:

BC1: $u(x, 0) = 0$.
BC2: $u(0, t) = U$ (a constant).

For these boundary conditions and stated assumptions, the solution is [2],

$$\frac{u(x,t)}{U} = \frac{1}{2}\exp(-xB)\,\mathrm{erfc}(A_1) + \frac{1}{2}\exp(xB)\,\mathrm{erfc}(A_2) \tag{10}$$

where

$$A_1 = \frac{x}{2\sqrt{\frac{D_{eff}t}{\varepsilon}}} - \sqrt{\frac{At}{\varepsilon}} \tag{10a}$$

$$A_2 = \frac{x}{2\sqrt{\frac{D_{eff}t}{\varepsilon}}} + \sqrt{\frac{At}{\varepsilon}} \tag{10b}$$

The partial pressure of oxidant does not appear in (10) because under the linearizing assumptions the increased tendency to penetrate is exactly compensated by the increased loss rate due to oxidation. The inherent reactivity (hence temperature dependence) appears within the definition of A and in D_{eff}. Also note that the stoichiometric constant, N_u, appears in A, hence affects both the penetration depth and speed of penetration.

Eq. (10) evolves toward the steady state solution (9) as $t \to \infty$. From the definitions of A_1 and A_2, the requirement is that

$\mathrm{erfc}(A_1) \to 2$ as $A_1 \to -\infty$, and
$\mathrm{erfc}(A_2) \to 0$ as $A_2 \to \infty$.

The complementary error function has this property: at $t = 0$, A_1 and $A_2 = \infty$, both $\mathrm{erfc}(A_1)$ and $\mathrm{erfc}(A_2) = 0$, satisfying BC1. As t increases, A_1 becomes negative and A_2 positive, $\mathrm{erfc}(A_1)$ tending toward 2 and $\mathrm{erfc}(A_2)$ tending toward 0, satisfying BC2.

5. Approximate D_{eff} values

Experiments conducted on British nuclear graphites [3–5], lead to a tentative form for the effective diffusivity,

$$D_{eff} = m(\alpha)D_{gas}. \tag{11a}$$

D_{eff} is offered as consisting of an internal geometry factor, $m(\alpha)$, α being the fractional oxidation, multiplied by the inherent diffusivity of the diffusing species. The experiments were conducted largely on counter-diffusing O_2/N_2 at low temperature and zero or low degrees of oxidation. As an overall net result, for low degree of oxidation, the measurements lead to the approximation,

$$D_{eff} = 0.01D_{gas}. \tag{11b}$$

Thus $m = 0.01$ is used in the ensuing calculations. There is recent information that German measurements show a smaller value of m, in the range $m = 0.001–0.007$ [6]. The effect of lower D_{eff} values than assumed by (11b) is discussed below in connection with Figs. 1–3. Also note that (11) contains a temperature dependence in D_{eff}, since D_{gas} increases with T approximately as $T^{1.5}$.

Use of D_{eff} to describe transport of a reactive species in a porous medium is a difficult concept, especially under oxidation conditions where a convective flux would be generated in addition to transport via concentration gradient. However there does not appear to be a practical alternative for general calculation purposes. Further discussion of British data and its implications is given in [1].

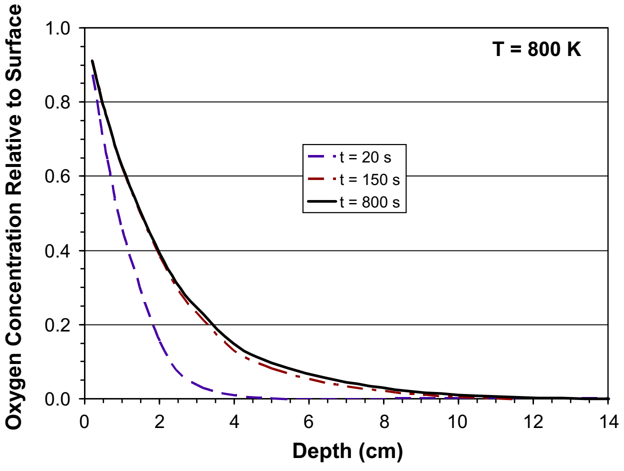

Fig. 1. Evolution of transient oxidant concentration profile (800 K, O_2 in N_2, $D_{eff} = 0.01D_{gas}$, $N_{O_2} = 1$).

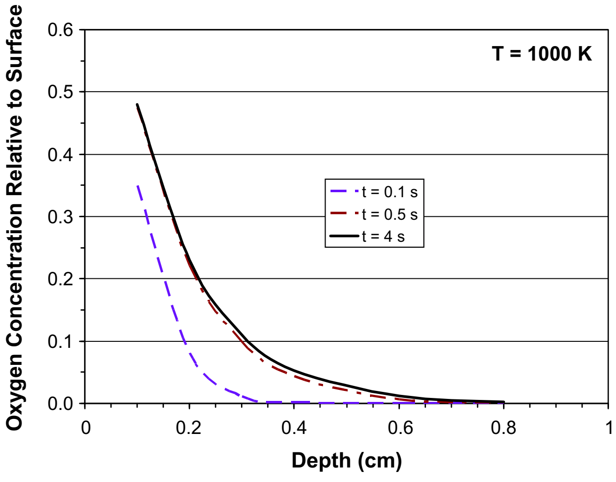

Fig. 2. Evolution of transient oxidant concentration profile (1000 K, O_2 in N_2, $D_{eff} = 0.01D_{gas}$, $N_{O_2} = 1$).

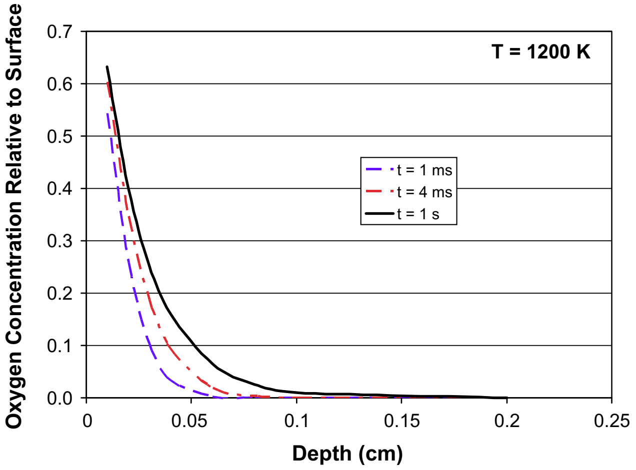

Fig. 3. Evolution of transient oxidant concentration profile (1200 K, O_2 in N_2, $D_{eff} = 0.01D_{gas}$, $N_{O_2} = 1$).

6. Transient O_2 concentration profiles

Transient profiles may be calculated using (10) given values for the linearized kinetics constants, and D_{eff} determined from (11b). A D_{gas} for O_2 in N_2 of 0.849 cm^2/s at 673 K is used with an assumed $T^{1.5}$ temperature dependence [7].[2] For kinetic constants we assume values determined by Contescu for oxidation in air,[3]

$$K_1 = 3.89 \times \exp(-186,960/RT) \qquad \text{mol C oxidized}/(\text{mol C s Pa}),$$

where activation energy is expressed in units of J/mol, and R and T are the gas constant (8.314 J/mol K) and absolute temperature (in K). Figs. 1–3 show transient O_2 concentration profiles for temperatures of 800, 1000, and 1200 K assuming $N_{O_2} = 1$, i.e., entirely CO_2 production, and $D_{eff} = 0.01D_{gas}$. Equilibration times may be estimated by observing convergence of these profiles, however a numerical method is given below.

At 800 K, equilibration is seen to be complete at about 150 s, judging from the equality of profiles at $t = 150$ s and $t = 800$ s at all locations. Note that a 95% penetration depth of 6.4 cm is estimated, defined as the depth at which the O_2 concentration drops to 5% of the surface value. (Penetration depths are discussed below.) At 1000 K, equilibration is seen to occur at about 4 s at all locations. The 95% penetration depth is reduced to about 0.4 cm. Transient curves for 1200 K show a 95% penetration depth of about 0.07 cm, too small for accurate measurement. Note in Figs. 1–3 (and more explicitly in Fig. 5) that the penetration depth diminishes with temperature. The reason is that the equilibrium profile results from the balance between the oxidant utilization rate, which tends to restrict penetration, and the rate of diffusion, as given by the diffusivity term. Since the oxidation rate increases with temperature more rapidly than D_{eff}, the oxidant loss rate gains in this competition as the temperature increases and the penetration depth decreases.

7. Numerical estimation of equilibration times for oxidation with O_2 and H_2O

Equilibration is essentially achieved when t increases to the point that $A_1 = -2$, at which point erfc(A_1) asymptotically ap-

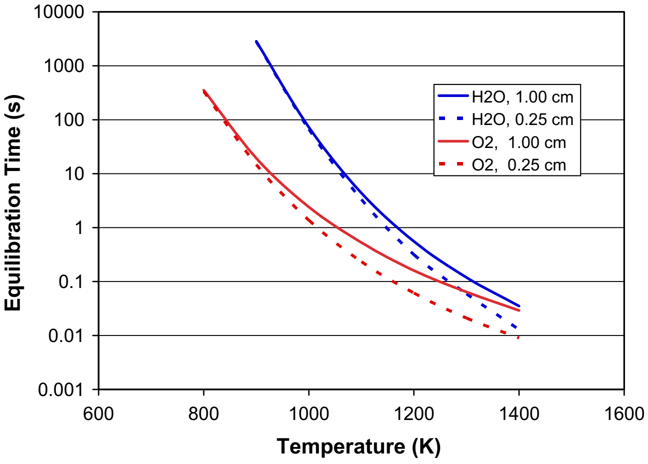

Fig. 4. Equilibration times vs. temperature for oxidation by O_2 and H_2O calculated at, depths of 0.25 and 1 cm ($D_{eff} = 0.01D_{gas}$).

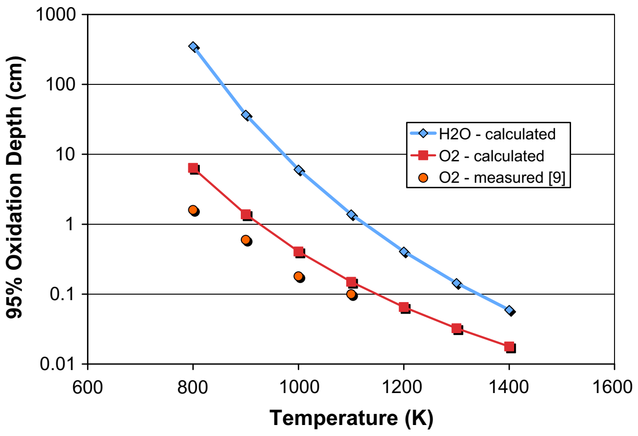

Fig. 5. Calculated 95% oxidation depths vs. temperature for oxidation by O_2 and H_2O; compared with oxidation in air measurements of Contescu et al. [9].

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[2] For comparison, for oxidation with O_2 in He, $D_{gas} = 2.822$ cm^2/s at 673 K, 3.32 times higher than for O_2/N_2. Since equilibrium penetration depths vary as $1/B$, therefore as $\sqrt{D_{eff}}$ at constant reactivity, 1.8 times greater equilibrium penetration depths are predicted for O_2/He relative to O_2/N_2.

[3] Contescu, personal communication of unpublished data to Wichner [1].

proaches its final value of 2.0, the equilibration condition. Thus the relation

$$A_1 = -2 \qquad (12a)$$

becomes the equilibration criterion, A_1 being defined by (10a). (12a) is a transcendental equation for time, t, which may be solved by iteration for a selected, x. By slight re-arrangement,

$$\sqrt{\frac{A}{\varepsilon}t} - 2\sqrt{t} - \frac{x}{2\sqrt{\frac{D_{eff}}{\varepsilon}}} = 0 \qquad (12b)$$

Since x must be specified, the equilibration time in principle differs for each depth. However, it will be seen, the difference is not significant at least for 0.25 and 1 cm depths.

For oxidation with H_2O, the linearized form of rate constants measured for oxidation of graphite H451 at low concentrations of water in He were used [8],

$$K_1 = 2000\exp(-274{,}000/RT) \qquad \mathrm{mol\,C\,oxidized}/(\mathrm{mol\,C\,s\,Pa})$$

The units of activation energy are J/mol and R and T are the gas constant and absolute temperature. The numerical value for activation energy was determined by empirical fit of oxidation rate data as reported in [8]. D_{gas} for H_2O in He was taken as 2.74 cm^2/s at 673 K [5]. As above, a $T^{1.5}$ temperature dependency of D_{gas} was assumed.

Criterion (12) was used to generate the equilibration times for H_2O and O_2 at depths of 0.25 and 1 cm shown in Fig. 4. As seen, equilibration times are relatively short for temperatures of 1000 K and above, at least out to 1 cm depth, for both O_2 (in N_2) and H_2O (in He) oxidation. As expected from its lower chemical reactivity, equilibration times are generally longer for H_2O. At 800 K, equilibration times approaching 4 days (3×10^6 s) are predicted for H_2O oxidation.

8. Oxidation depth

The equilibrium e-folding depth, i.e., the depth at which $u/U = 1/e$ at large t, is obtained directly from (9),

$$X_\varepsilon = 1/B. \qquad (13a)$$

More useful is the equilibrium depth at which the oxidant concentration drops to some specified fraction, β. From (9),

$$X_\beta = -\ln(\beta)/B. \qquad (13b)$$

X_β may be estimated from (13b) using kinetic constants and D_{eff} required for estimation of B.

Fig. 5 shows equilibrium penetration depths for H_2O and O_2 oxidation as a function of temperature, assuming a 95% penetration depth. Note that as a result of its lower oxidation rate, H_2O penetrations are consistently greater than for O_2. A quite large penetration of about 350 cm is predicted for H_2O at 800 K. Such large depths determined for a semi-infinite slab implies an essentially flat profile for smaller graphite members at 800 K and below (see further, Ref. [1]). Fig. 5 also shows that calculated 95% penetration depths for O_2 compare reasonably well with reported density profile measurements of Contescu et al. [9] obtained by successive machining and weighing of thin slices (1 mm) from specimens oxidized in controlled conditions. It is noteworthy that the calculated and measured temperature trends follow closely.

Eq. (13) may be used to illustrate the effect of smaller values for D_{eff} reported from a German source [6]. From the definition of B from (8) and (6) it is seen that B increases with diminishing D_{eff}. Consequently from (13), the penetration depth will decrease with decreasing D_{eff}, a result readily arrived at intuitively.

Fig. 5 shows that the temperature trend of the penetration depth is accurately reproduced by the analytical development and, at least for the illustrated case, predicted penetration depths agree reasonably well with a measured density profile.

From the definition of B, it can be shown that the predominant temperature trend of penetration depth is,

$$X_\beta \approx \exp(H/2RT),$$

where H is the activation energy of the oxidation reaction. Other temperature dependencies in B cause departure from this relation, as illustrated by the curves in Fig. 5, but it is approached at high temperature.

The reasonable agreement in the penetration depths and the close agreement in the temperature trend indicate that the main assumptions yield fairly realistic results.

9. Summary

An analytically solvable differential equation for the transient oxidation of a graphite slab is obtained under the assumptions of constant graphite density and linearized oxidation kinetics. Also required is an expression for the effective diffusivity of oxidant. This was approximated by a two-factor expression based on low temperature measurements at low, or zero weight-loss.

Equilibration times may be estimated by viewing the convergence of transient curves, or more conveniently, by an iterative solution of a transcendental equation. In general, equilibration times differ for differing depths, but differences appear to be small between depths of 0.25 and 1 cm. Equilibration times are quite short for 1000 K and above, but increase rapidly at lower temperatures, approaching about 4.6 days for H_2O at 800 K.

The transient profiles converge to the equilibrium profile at large t, from which equilibrium penetration depths may be estimated. As shown, penetration depths depend on the value of a materials parameter, B, which includes the kinetic constants, effective diffusivity, and a stoichiometric constant. Predicted equilibrium depths for oxidation by O_2 compare reasonably well with published data.

Acknowledgments

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