R. D. Burnette, C. Velasquez, G. Hightower and K. Koyama General Atomic Company

INTRODUCTION

The thermally induced oxidation of nuclear grade graphites by steam at temperatures around 1000° C is controlled by both mass transport and reaction kinetics. This complication has given rise to a number of theoretical treatments (1, 2, 3, 4) which describe simultaneous diffusion and chemical reaction in the porous media. This paper utilizes a model advanced by Dodson⁽⁴⁾ and compares it to experimental results for ATJ nuclear graphite. In this study the parameters surface-to-volume ratio, temperature, concentration and in-pore diffusion were considered.

THEORY

It is generally concluded that thermally induced oxidation of graphite proceeds by the following steps: (1) in-pore gas phase diffusion of reactant to active sites, (2) chemisorption, (3) chemical reaction and (4) desorption and diffusion of products out of the porous media. The present theoretical treatment neglects the final step in this process, assuming that reactant diffusion, chemisorption and chemical reaction are rate controlling. The equation of Dodson describing simultaneous diffusion and chemical reaction in a porous media was re-defined to give a general solution for total rate of oxidation: i.e.,

$$R_{T} = S/V L F_{i} R_{s}$$
(1)

where: R_T is the total reaction rate of the sample, s⁻¹, S/V is the surface-to-volume ratio of the graphite specimen, cm_1^{-1} , L is the "diffusion length" given by $(D_{eff}/K_V)^{\frac{1}{2}}$ where D_{eff} is the effective diffusion coefficient for water vapor in the porous media given by $D_{eff} = mD_{1,2}$ where $D_{1,2}$ is the diffusion coefficient of H_2O in He and m is a constant characteristic of the porosity and tortuosity of the graphite. K_V is the volumetric reaction rate constant, s⁻¹, defined as: $K_V = R_S \rho RT/12 P_{H_2O}$. F_i is a geometrical effectiveness factor. For the cylindrical samples used in this study:

$$F_{i} = \frac{I_{1}(R_{o}, L)}{I_{o}(r_{o}/L)}$$
(2)

where I₁ I₀ are modified bessel functions first kind, first and zero order, respectively, r₀ is the radius of the cylinder. R_s is the chemical surface reaction rate in the absence of mass transport control, frac/ sec. R_s in this study is shown to be described adequately by a Langmuir type equation as given in the results section. A useful result of these formulae is the relation

$$\frac{C}{C_o} = \frac{I_o}{I_o} \frac{(r/L)}{(r_o/L)}$$
(3)

where C_0 is the water vapor concentration at the surface of the sample or r_0 and C is the concentration at radius = r.

EXPERIMENTAL

Samples were trepanned from ATJ production

graphite blocks as supplied by Union Carbide. They were machined to the desired geometry, then ultrasonically cleaned in acetone to remove residual graphite dust, organic or other impurities, dried in an oven at 100°C and weighed. Oxidation rate measurements were performed with use of automatic recording microbalances. Reaction rates were calculated from weight loss versus time data. Test samples were suspended from the balance beam by means of a platinum wire, inside a gas tight quartz hangdown tube positioned inside a resistively heated SCR controlled furnace. Helium was passed over the samples at flow rates ranging from 100 to 1000 cc/min (linear velocities of 0.4 to 4 cm/sec. Above 300 cc/min the increase in rate of oxidation approached zero order with respect to flow, thus rate studies were conducted at 300 to 500 cc/min. Various moisture levels from 200 to 30,000 µatm were obtained by blending dry helium with water saturated helium via the use of calibrated flowmeters. Moisture concentrations were monitored with either a MEECO electrolytic type (range 1-1000 ppmv) or an EG&G Model 880 dewpoint type (range 1000-30,000 ppmv) moisture monitor. Hydrogen concentrations from 500 to 10,000 µatm were obtained by the use of premixed cylinders. ATJ test samples were right circular cylinders 3.8 cm long having diameters of 0.64, 1.3, 1.9, 2.5, and 3.2 cm, and having S/V of 6.8, 3.6, 2.6, 2.1 and 1.8 cm⁻¹ respectively. In addition thin slabs were used, $0.32x^2.5x^3.5x^3$.0 cm, S/V = 7.5 cm⁻¹. The thin slabs and small cylinders were used to determine ${\rm R}_{\rm S}$ or ${\rm K}_{\rm V}.~$ The larger cylinders were used to determine the mass transport parameter m.

RESULTS AND DISCUSSION

It was found that the local isothermal chemical reactivity of thin slabs or cylinders of ATJ graphite was generally described by:

$$R_{s} = \frac{F_{b}K_{1}P_{H_{2}0}^{0.9}}{1+K_{2}P_{H_{2}}} \qquad (sec^{-1})$$
(4)

where $F_{b} = a$ factor to normalize burnoff

$$K_{1} = \frac{3.65 \times 10^{11}}{T} \exp(68000/RT) \text{ (sec}^{-1} \text{ atm}^{-0.9})$$

$$K_{2} = \frac{4.51 \times 10^{3}}{T} \exp(14500/RT)$$

The thermally dependent constants K_1 and K_2 determined at 1% burnoff are similar to those obtained by Everett et al., (Ref. 3) in studies of G-5 nuclear grade graphite. A plot of R_s vs 1/T is given in Fig. 1 where the experimental data points are compared with the rate expression, equation (4).

By plotting the overall reaction rates obtained at $980^{\circ}C$ expressed as a surface oriented process, mg/ cm² sec vs S/V, it was determined that for S/V below 3.6 cm⁻¹, (Dia.>1.3 cm) the reaction rate per cm² was relatively constant, indicating that F₁ in Eq. 1 was essentially 1. The diffusion parameter m was determined by substituting into Eq. 1 values of K_V obtained from the experiments using the thin slabs and cylinders. The values of m for all the ATJ graphite samples ranged from 0.002 to 0.003. A plot of log P_{H_2O} vs. log rate is shown in Fig. 2 for the largest specimen used, 3.2 cm dia. The solid lines, were calculated from the theoretical Eq. 1 using the reaction rate data and m factors previously determined. Figure 3 is a plot of log H₂ concentration vs log rate showing the excellent correlation with calculated lines.

A long term proof test was performed in which a 2.5 cm dia. ATJ cylinder was oxidized to 16% weight loss at conditions designed to give a non-uniform oxidation profile. The burnoff profile of the oxidized sample was determined with the use of a lathe technique and compared to the predicted profile calculated using a modified form of Eq. 3. The results of this comparison shown in Fig. 4, and indicate remarkable agreement between the calculated and experimental results.

CONCLUSIONS

The steam oxidation characteristics of ATJ graphite has been shown to correlate well with a simple general relation describing simultaneous diffusion and chemical reaction. It was found that the reaction kinetics were adequately described by a Langmuir type equation. Reactant transport in the porous media is shown to be correlated by a semi-empirical factor, m, applied to the ordinary gas phase diffusion coefficient.

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Fig. 1



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