

Oxidation Kinetics Study on HTGR Graphites, 2020 and PGX

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Abstract

Oxidation kinetics for HTGR graphites, 2020 and PGX were studied as a function of P_{H_2O} and P_{H_2} at 850°C with large sized block-shaped specimens in a closed system. The results can be represented by an existing rate equation successfully.

Introduction

The ability to predict the oxidation rates for the graphite components in a High Temperature Gas Cooled Reactor (HTGR) under normal operation condition as a function of time (up to 40 years) and under an accidental condition, is needed to estimate the strength loss of the graphite caused by oxidation, and also to calculate the impurities levels in the He coolant.

Gadsby et al.¹ showed that the primary product of steam-carbon reaction is carbon monoxide, and that the rate can be represented by an expression,

$$R(\text{rate}) = \frac{k_1 P_{H_2O}}{1 + k_2 P_{H_2} + k_3 P_{H_2O}}$$

Later, Giberson and Walker² proposed an equation,

$$R = \frac{k_1 P_{H_2O}}{1 + k_2 P_{H_2}^{1/2} + k_3 P_{H_2O}}$$

with a mechanism involving the dissociative adsorption of hydrogen on graphite. When the effects of burnoff (F_b) and catalysis (F_c) are incorporated, the equation becomes,

$$R = \frac{k_1 P_{H_2O} \cdot F}{1 + k_2 P_{H_2}^{1/2} + k_3 P_{H_2O}} \quad (1)$$

where F is $F_c \times F_b$.

To determine the reaction constants by experiments, thin disk specimens are usually used to minimize the effect of in-pore diffusion on the observed reaction rates. However, using a small sample introduces the necessity for high sensitivity

in measurement and the dangers of exaggerated effects of burnoff and catalysis. Ideally, two sets of data from thin disk samples and large samples should be obtained and compared to understand the in-pore diffusion on the reaction rates, assuming that the data from large samples also follow the relationship discussed above. No systematic study on oxidation kinetics of HTGR graphites using large sized samples has been conducted, and it was attempted to demonstrate the needs for and benefits of this approach, and at the same time, to measure the reaction constants for 2020 (Stackpole Carbon Corp.) and PGX (Union Carbide) graphites.

Experimental

Block shaped (15.24 cm x 5.97 cm x 5.72 cm) 2020 and PGX graphites were used for the experiments. The oxidation rates were measured as a function of time at 850°C with the initial gas composition of 500 ppm H_2O /5000 ppm H_2 /balance He. Product gases CO , CO_2 and CH_4 were monitored via infrared detectors and H_2 and H_2O were determined by gas chromatography and dew point measurement, respectively. After a certain period of oxidation, the oxidation rate stays almost constant and the H_2O level was varied between 5×10^{-4} atm and 3×10^{-3} atm. H_2 level was also varied between 1×10^{-4} atm and 1.5×10^{-2} atm, while maintaining the H_2O level at 5×10^{-4} atm. More detailed information can be found elsewhere.³

Discussion

Since one of the purposes of this paper is to show whether the oxidation rates of impure graphites such as 2020 and PGX can be expressed by Eq. (1), F for 2020 graphite was put as 1. (The exact value for F is not available at the time of writing, and does not affect the results of this discussion.) Equation (1) can be rewritten as

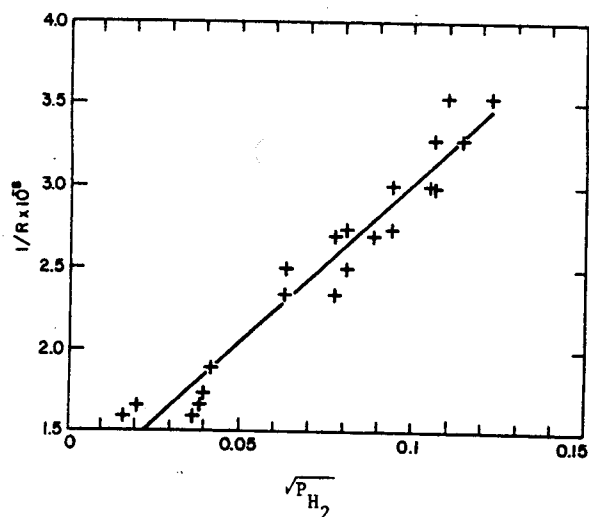


Figure 1. Oxidation rate of 2020 graphite as a function of P_{H_2} (atm) at $P_{H_2} = 5 \times 10^{-4}$ atm at 850°C .

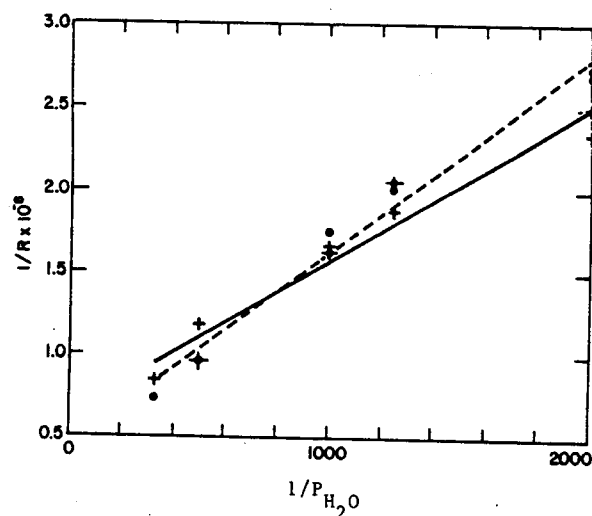


Figure 2. Oxidation rate of 2020 graphite as a function of P_{H_2O} at 850°C .
 •: $P_{H_2} = 7.5 \times 10^{-3} \sim 8 \times 10^{-3}$ atm,
 +: $P_{H_2} = 4.3 \times 10^{-3} \sim 5.0 \times 10^{-3}$ atm.

$$\frac{1}{R} = \frac{k_2}{k_1 P_{H_2O}} \cdot P_{H_2}^{1/2} + \frac{1}{k_1} \left(\frac{1}{P_{H_2O}} + k_3 \right). \quad (2)$$

From a plot of $1/R$ vs. $P_{H_2}^{1/2}$, two relationships between k_1 , k_2 and k_3 can be obtained. Equation (2) can be rearranged as

$$\frac{1}{R} = \frac{k_3}{k_1} + \frac{1 + k_2 P_{H_2}^{1/2}}{k_1} \cdot \frac{1}{P_{H_2O}}.$$

From a plot of $1/R$ vs. $1/P_{H_2O}$, two more relationships can be obtained. Since we used two levels of P_{H_2} in this study, we have five equations and three unknowns. For the plots, only CO production was considered, and CO levels were converted to weight loss in $\text{g/cm}^2/\text{sec}$. For 2020 graphite, the slope and intercept from a plot of $1/R$ vs. $P_{H_2}^{1/2}$ (Figure 1), and the intercept value of 5×10^7 from the plots of $1/R$ vs. $1/P_{H_2O}$ (Figure 2) was used to solve for k_1 , k_2 and k_3 . These k values were then used to calculate the slopes for the plots of $1/R$ vs. $1/P_{H_2O}$. The calculated slopes and the observed ones are compared in Table 1. The agreements are very good.

Table 1. Comparisons of Calculated and Observed Slopes

| Grade | P_{H_2} (atm) | Slope in $1/R$ vs. $1/P_{H_2O}$ | |
|-------|----------------------|---------------------------------|---------------------|
| | | Calculated | Observed |
| 2020 | 4.5×10^{-3} | 9.39×10^4 | 9.27×10^4 |
| | 8×10^{-3} | 1.16×10^5 | 1.195×10^5 |

For PGX graphite oxidized in $P_{H_2} = 5 \times 10^{-3}$ atm and $P_{H_2O} = 5 \times 10^{-4} - 3 \times 10^{-3}$ atm, when F value of 17.5 was used, the resulting slope and intercept in a plot of $1/R$ vs. $1/P_{H_2O}$ agreed with those from 2020 graphite as shown in Table 2. Again, the agreements are very good.

Table 2. Comparisons of Slopes and Intercepts for 2020 and PGX Graphites

| Grade | Slope | Intercept |
|--------------------|---------------------|--------------------|
| 2020 | 9.26×10^4 | 6.48×10^7 |
| PGX, $F = 17.5$ | 9.298×10^4 | 5.73×10^7 |

Conclusions

1. The oxidation rates for 2020 graphite at 850°C can be represented by the Gadsby-Hinshelwood type equation.
2. The oxidation rates for PGX graphite in environments with $H_2/H_2O = 1.7-10$ at 850°C can also be represented by the Gadsby-Hinshelwood type equation.
3. It is more realistic using the oxidation kinetics data generated from large sized graphite samples than using those from thin samples in predicting the oxidation kinetics for the graphite components in the HTGR's under different conditions, and the quality of the data from large samples may be better than that from small sized samples.

Acknowledgments

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References

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