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AN EVALUATION OF THE SIGNIFICANCE OF INVERSE OXIDATION FOR HTGR GRAPHITES

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1. Introduction

Walker and his co-workers[1] have observed the inverse oxidation phenomenon following gasification of graphite cylinders to relatively high burnoffs. The inverse oxidation refers to a higher mass loss inside the graphite than the outside. In 1980, Wichner et al[2] reported this phenomenon (referred to as inside/out corrosion) observed in some H451 graphites, and offered an explanation that a catalyst (almost certainly Fe) is activated by the progressively increasing reducing conditions found in the graphite interior. Recently, Morgan and Thomas[3] (1982) investigated this phenomenon in PGX graphites, and agreed on the existing mechanism to explain this phenomenon. They also called for attention to the possibility that this phenomenon may occur under HTGR (High Temperature Gas-Cooled Reactor) operating conditions.

The purpose of this paper is to confirm the above mentioned explanation for this phenomenon and to evaluate the significance of this effect for HTGR graphites under realistic reactor conditions.

2. Discussion

Morgan and Thomas[3] oxidized PGX graphite blocks (115 x 165 x 190 mm) in 80% CO_2/20% CO at 875°C and observed an inverse oxidation. Two other grades of graphites (P3W and ATJ) also showed similar behaviors. Auger electron spectroscopy (AES) showed that the impurities at the bottom of the voids formed by oxidation are mainly iron, sulfur and calcium. They proposed the same explanation that was given by Walker et al[1] and Wichner et al[2] for the observed inverse oxidation; the limited access of CO_2 to the interior of the graphite against the countercurrent of CO causes a higher ratio of CO/CO_2 inside the graphite than outside and, as a result, FeO is reduced at a certain distance from the surface to Fe that accelerates the oxidation reaction through catalysis.

For the oxidation of Fe in a CO/CO_2 gas mixture,

$$Fe + CO_2 \rightleftarrows FeO + CO, \Delta G^\circ = 4900 - 5.25T.\dagger \quad (1)$$

At T = 875°C,

$$R^* (CO/CO_2) = \left(\frac{P_{CO}}{P_{CO_2}}\right)^* = \exp\left(\frac{-\Delta G^\circ}{RT}\right) = \underline{1.64},$$

where ΔG° is a standard free energy change for the reaction, R is a gas constant and R^* (CO/CO^2) is the equilibrium CO/CO_2 ratio.

For the oxidation of FeO to Fe_3O_4 in a CO/CO_2 gas mixture,

$$3FeO + CO_2 = FeO + CO \quad \Delta G^\circ = -7550 + 9.2T\dagger \quad (2)$$

At T = 875°C,

$$R^* (CO/CO_2) = \left(\frac{P_{CO}}{P_{CO_2}}\right)^* = \exp\left(\frac{-\Delta G^\circ}{RT}\right) = 0.267.$$

Morgan and Thomas used a gas ratio,

$$\frac{P_{CO}}{P_{CO_2}} = 0.25$$

which is close to the equilibrium gas ratio for FeO/Fe_3O_4. Thus, the outer part of the sample probably contained FeO, and as the oxidation proceeded the ratio $\left(\frac{P_{CO}}{P_{CO_2}}\right)$ increased and reached the R^* value of ~1.67 that converted FeO to Fe. As a result, oxidation accelerated at a distance that was determined by the diffusion rates of CO_2 and CO, and showed the inverse oxidation phenomenon.

At the Brookhaven National Laboratory,[5] the effect of the gas ratio, $\frac{P_{H_2}}{P_{H_2O}}$, on the reaction rate of PGX graphite containing about 100 ppm Fe at four different temperatures was studied and the results are shown in Figures 1 and 2. The gas ratio was changed by adding H_2 gas to an atmosphere of 0.63% H_2O in He.

For the reduction of FeO in a H_2/H_2O gas mixture, the free energy change is

$$Fe + H_2O \rightleftarrows FeO + H_2 \quad \Delta G^\circ = -3150 + 1.85T\dagger \quad (3)$$

the calculated equilibrium gas ratios are ~1.64, ~1.5 and ~1.37 for 760°C, 857°C and 956°C, respectively.

† Thermodynamic values are from Ref. 4.

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