

THE KINETIC DEPENDENCE OF IRON CATALYZED GRAPHITE OXIDATION ON OXYGEN POTENTIAL*

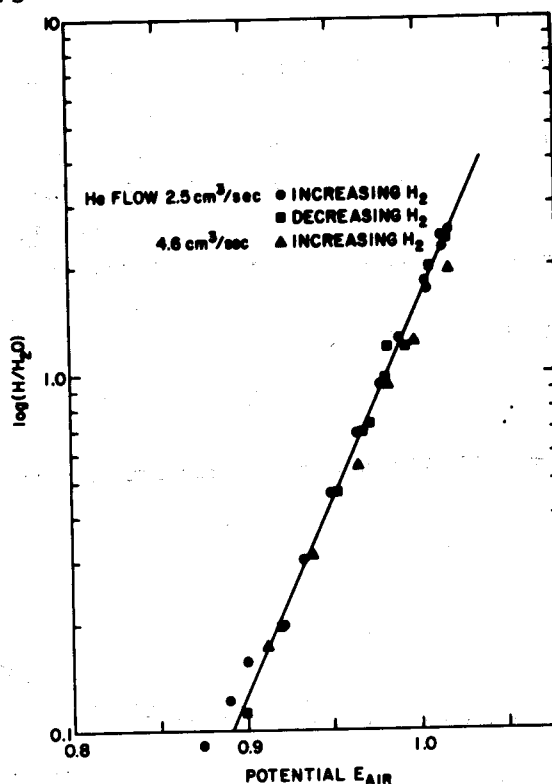
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The influence of gaseous components on the rate of oxidation of pure graphite is relatively well understood and has been presented analytically.(1) With impure graphites, the dependence is more complex. Some impurities catalyze the oxidation but give the same dependence on gaseous concentrations, (1) and others, e.g., iron which causes marked rate changes with small changes in gas composition, (2) but no quantitative information was available as to how rapidly these rates changed with gas composition. This work describes measurements of rates as a function of the oxygen activity or potential.

The apparatus consisted of an electrobalance to measure the weight of graphite suspended in a furnace. The iron impregnated graphite was prepared from high purity nuclear graphite. Helium was used with controlled hydrogen to water concentration ratios. After passing over the specimen, the oxygen potential of the gas was measured using an electrochemical oxygen meter at 650°C with air as a reference. The calibration of the meter in terms of the H_2/H_2O ratio is shown as a functional potential in Figure 1. This logarithmic curve was in excellent agreement with that calculated from thermodynamic data.

(1) M. B. Perroomian, et al, Report No. GA-A12493, January 1974.

(2) P. L. Walker, Jr., et al, Chem. & Phys. of Carbon, Vol. 4, 287 (1968).

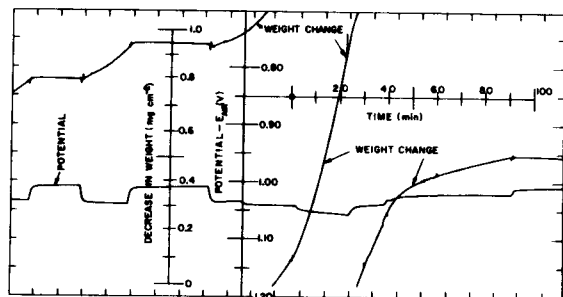


RELATIONSHIP BETWEEN POTENTIAL AND
 H_2/H_2O RATIO

The effect of changes in gas composition on the weight and oxygen potential are shown in Figure 2 for a high (15%) burnoff sample. Rapid potential changes followed changes in the helium composition but measurements showed a potential of -1.02 volts was critical. When the potential was less negative, no oxidation was evident, while when more negative, the graphite began oxidizing. The oxidation could, therefore, be turned off and on as the gas composition was changed. This potential is close to the oxygen potential at which iron and

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wustite are in equilibrium, and significantly less than that corresponding to magnetite and wustite equilibrium. The results are, hence, in agreement with a model where the oxidation is catalyzed by iron but not by wustite.

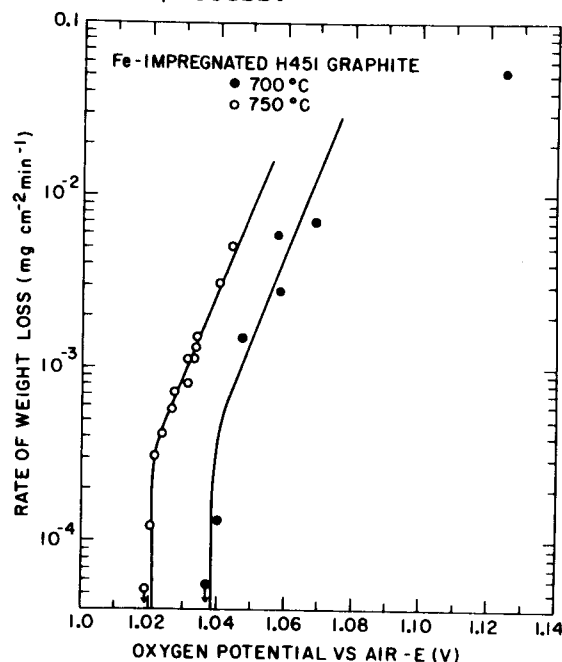


POTENTIAL AND WEIGHT CHANGE WITH TIME FOR 15% BURNOFF IRON IMPREGNATED GRAPHITE

Figure 2 also showed that when the potential decreased progressively below -1.02, the rate of oxidation continued to increase. This behavior was found to be reproducible both qualitatively and quantitatively and can be seen in Figure 2. The results in Figure 3 show the relationship between potential and oxidation rate for 750°C. At potentials just below the critical value, the rate of oxidation changed rapidly and then increases logarithmically with potential. A similar behavior was observed at 700°C for ~15% burnoff samples. As the relationship between the rate and the potential is logarithmic, it can simply be shown that the rate of oxidation is related to the oxygen activity or H_2/H_2O ratio. The slopes

for the respective logarithmic relationships indicated that the rate of oxidation of the iron containing graphite increases approximately with the square of the H_2/H_2O ratio or with the reciprocal of the oxygen activity to the fourth power. With high purity graphite, the rate of oxidation by water vapor is inhibited by the presence of hydrogen in contrast to the observations presented here, indicat-

ing in the presence of iron, hydrogen acts as a strong stimulant for the oxidation process.



EFFECT OF POTENTIAL ON OXIDATION RATE

The same rapid response to changes in the oxygen potential with iron impregnated graphite with low burnoff and on impure graphites containing iron, was not observed. The fine pore structure in the low burnoff sample prevented rapid exchange between the gases within and external to the specimen, and rates could not be controlled. The impurities, other than iron, catalyzed the oxidation and gave a background of hydrogen as well as a continued rate of oxidation at all oxygen activities tested. These results were, nevertheless, in agreement with those presented for the high burnoff specimen but were complicated by the gas composition changes with depth in the graphite.