THE OXIDATION OF GRAPHITE UNDER COMPRESSIVE STRESS*

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Introduction

In recent years data has been published showing a large effect of tensile stress on the oxidation rate of graphite in argon with small additions of water vapor (1,2). This work was undertaken primarily to determine the effect of compressive stress on such a reaction. In the course of the work, other factors affecting gasification rate, such as temperature, flow rate and concentrations of inhibiting species are also being investigated.

Experimental

Graphite samples in the form of right cylinders 0.75" diameter and 1.50" long were cut from blocks of Stackpole 2020 and Great Lakes H440 graphite and were held between an alumina anvil and ram. The load was applied via a lever arm by a simple dead weight loading technique. The sample was placed in a vertical tube furnace with a bellows arrangement at the top to allow load to be transmitted to the sample. The load was measured using a Tyco 1000 pound load cell.

He-CO and He-CO_2 gas mixtures were obtained by combining gas from cylinders of He, He + 1000 ppm CO and He + 1000 ppm CO_2. Water vapor was added to the gas stream by passing it over ice in a refrigerated bath whose temperature was varied to change H_2O concentration. During any run six parameters were continuously monitored viz., furnace and sample temperatures, compressive load, and the concentrations of CO_2, CO and H_2O in either the inflowing or outflowing gas stream. H_2O concentration was measured using a Beckman trace moisture analyzer and CO and CO_2 concentrations were measured using Beckman infrared gas analyzers. The respective accuracies were ± 5% and ± 1%. The data collected were recorded using a six point recorder.

Effect of Compressive Loading

In no case investigated so far has there been the slightest hint of any effect of compressive loading on reaction rate. A summary of some of the data obtained using Stackpole 2020 graphite is given in Table 1. Gas concentrations are given to the nearest 5 ppm but in most cases the accuracy of measurement was slightly better than that. In all cases in which a He-CO_2 reactant gas mixture was used there was conservation of oxygen.

The compressive strength (σ_c) of Stackpole 2020 graphite is around 12,000 psi so that the loads applied here are $<\sigma_c/20$, however even when the experimenter's own weight was added to the load to give a stress of $\sim\sigma_c/7$ there was still no effect on reaction rate!

A typical data output for the C-H_2O reaction is shown in Figure 1. There are very slight variations in gas concentrations during the run but no sign of any effect of stress. The original Euratom Petten work on this effect by Krefeld et al.,[1,2] differed from our investigations in that tensile stresses were used. Effects were observed at 1000°C with only 20 ppm H_2O present and stresses of 350 psi were sufficient to produce the maximum effect, which consisted of a 2-7 fold increase in the concentrations of reaction products.

Duplication of Krefeld's work (3) has been attempted by other workers using an identical apparatus and the same graphite material as that for which Krefeld found the largest effect, in addition to other materials. In no case was any effect of tensile stress on oxidation found.

No model which can qualitatively explain Krefeld et al.'s results (viz. pore opening or impurity migration due to the stress field) would predict zero effect for compressive stress. Our results are obviously inconsistent with those of Krefeld et al. In addition to the different mode of stress there is a major difference in the gas flow rates (33,000 - 55,000 ml/hr vs 200 ml/hr). Lower flow rates cannot be used in our apparatus because of the requirements of the infrared gas analyzers.

Table 1

Sample Temp. (°C)	Stress Comp. (psi)	$X^{in}_{CO_2}$ (ppm)	$X^{in}_{H_2O}$ (ppm)	$X^{out}_{CO_2}$ (ppm)	X^{out}_{CO} (ppm)
888	0	85	-	60	45
	267	85	-	60	45
	362	85	-	60	45
888	0	175	-	135	80
	267	175	-	135	80
	362	175	-	135	80
893	0	-	885	75	125
	267	-	885	75	125
	362	-	885	75	125
	456	-	885	75	125
908	0	115	-	85	60
	456	115	-	85	60
	650	115	-	85	60
908	0	-	125	15	30
	362	-	125	15	30
	456	-	125	15	30

Effect of Gas Flow Rate on Oxidation

Using the apparatus designed for examining oxidation under stress it has been possible to commence investigations into the effect of gas flow rate on oxidation rate. The exact flow rates used were 9.2, 13.8 and 15.3 ml/sec corresponding to velocities of 2.1, 3.2 and 3.6 mm/sec past the sample.

Reaction rates are calculated using the first order rate equation given by Hedden and Löwe[4] for their "open circuit" oxidation experiments. For the graphite - CO_2 reaction the rate is given by

$$-\frac{dr_c}{dt} = V_{in}(X^{in}_{CO_2} - X^{out}_{CO_2}) \frac{P_{total}}{82.05\ T_{room}\ (K)}$$

where $-dr_c/dt$ is the number of moles of carbon consumed per second, V_{in} is the gas flow rate in cm^3/sec and $X^{in}_{CO_2}$ and $X^{out}_{CO_2}$ are the inlet and outlet mole fractions of CO_2. P_{total} is one atmosphere.

For the graphite -H_2O reaction the rate is

$$-\frac{dr_c}{dt} = V_{in}(X^{out}_{CO_2} + X^{out}_{CO}) \frac{P_{total}}{82.05\ T_{room}\ (K)}$$

where X^{out}_{CO} is the mole fraction of CO in the outlet gas.

Reaction rates as defined in the above equations are plotted as functions of the inlet CO_2 and H_2O partial pressures (mm Hg) in Figures 2 and 3. The three curves on each figure correspond to the three flow rates used. It can be seen that for any given partial pressure the rates increase on increasing the flow rate from 9.2 ml/sec to 13.8 ml/sec but decrease when the flow rate is further increased to 15.3 ml/sec. These results are somewhat mysterious and further investigation is necessary. However the same effect is found for both the C-H_2O and C-CO_2 reactions and there is no reason to doubt its validity at present.

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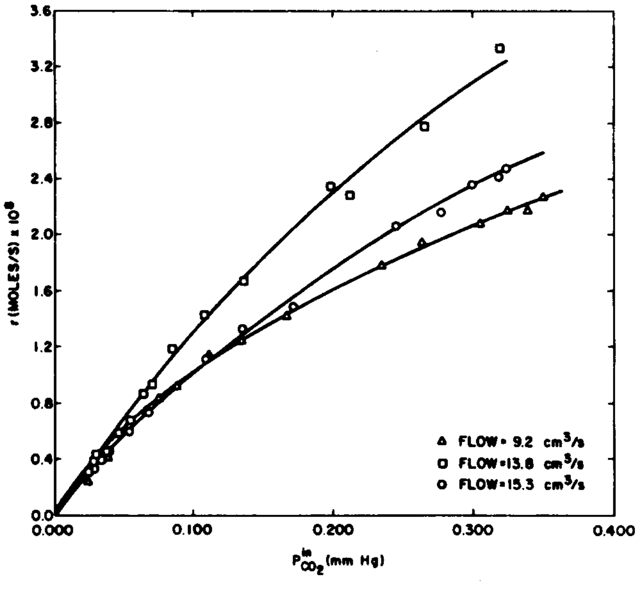

Fig. 2 Reaction rate of Stackpole 2020 graphite versus partial pressure of CO_2 in the inlet gas at 893°C for different flow rates.

References

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2. R. Krefeld, G. Linkenheil, and W. Karcher, ORNL-CONF-730601, p. 88 (1973).
3. Heinrich and Weimann, (HRB, Mannheim) private communication.
4. K. Hedden and A. Löwe, Dragon Project Report #205 (1963).

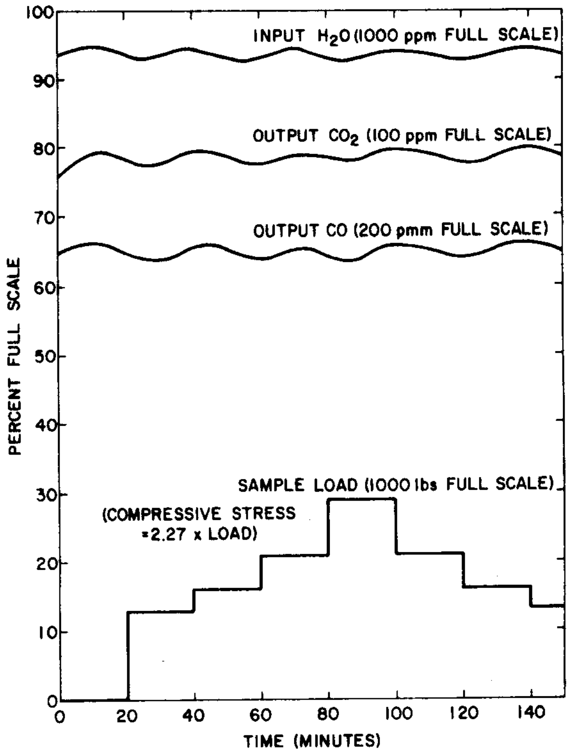

Fig. 1 Typical data output for Stackpole 2020 graphite oxidized in helium containing 930 ppm H_2O under different compressive loads.

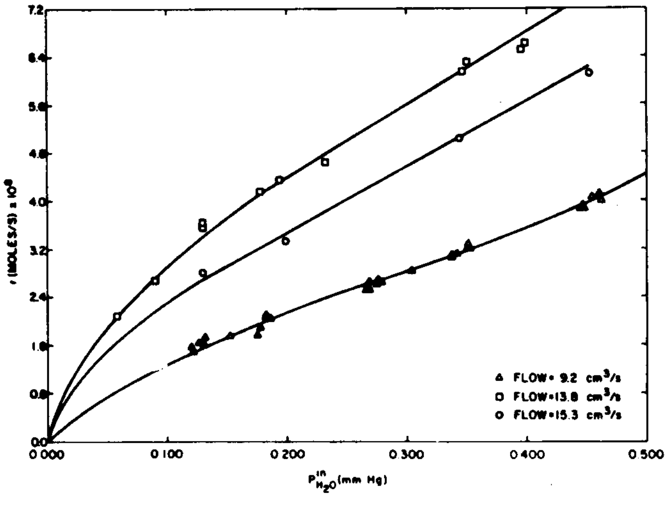

Fig. 3 Reaction rate of Stackpole 2020 graphite versus partial pressure of H_2O in the inlet gas at 893°C for different flow rates.