

## REACTION OF GLASSY CARBON WITH OXYGEN

F. RODRIGUEZ-REINOSO\* and P. L. WALKER, JR.

Department of Material Sciences, The Pennsylvania State University, University Park, Pennsylvania 16802, U.S.A.

(Received 10 June 1974)

**Abstract**—A glassy carbon, GC-30, from Tokai Electrode Manufacturing Co., Ltd. has been reacted in O<sub>2</sub> between 750 and 850°C. At low carbon burn-offs the reaction has an activation energy of  $63 \pm 3$  kcal/mole. Changes in dimensions of samples as a function of burn-off at 900°C were studied. Dimensional changes are compared with those resulting from the oxidation of highly oriented pyrolytic graphite. For comparable sample shapes, glassy carbon is more reactive than highly oriented pyrolytic graphite.

## 1. INTRODUCTION

Although glassy carbons have been available for about ten years and the number of applications is continuously growing, it is surprising how little the kinetics of its reaction with O<sub>2</sub> has been studied. Most of the work reported concerns the oxidation of glassy carbon in air[1-3], CO<sub>2</sub>[4], and other compounds[1-5]. Results in dry air[3] show that the reactivity of glassy carbon is lower than that of electrode and pyrolytic graphites. These results are expressed as weight loss per square centimeter, although it is not specified if it is total or geometric area. Since the oxidation of highly oriented pyrolytic graphite in O<sub>2</sub> has been previously studied in this laboratory[6, 7], it was considered fruitful to compare these reactivity results with those found for glassy carbon under similar conditions.

## 2. EXPERIMENTAL

The material used was a glassy carbon, designated GC-30 and supplied by Tokai Electrode Manufacturing Co., Ltd., heat treated at 3000°C. Physical properties of this material are discussed in detail elsewhere[5]. From the original plate of glassy carbon, which was 1 mm in thickness, several samples were obtained by simply breaking it, in order to avoid contact with any cutting device which might introduce impurities. The dimensions were carefully measured using a precision micrometer. The thickness of 1 mm was constant for all samples used and the total area was kept as similar as possible at about 2.5 cm<sup>2</sup>. The top and bottom surfaces of the plate constituted about 80 per cent of this area.

Samples were suspended by a quartz fiber from a Cahn RG electrobalance, using an experimental apparatus

described in detail elsewhere[6]. The O<sub>2</sub> used was "ultrapure" grade supplied by the J. T. Baker Company. Samples were outgassed at about  $5 \times 10^{-6}$  Torr, using a Vacfon pump for 8 hr at 950°C prior to reaction. The temperature was then lowered to that desired for reaction and allowed to stabilize before O<sub>2</sub> was admitted to the system. Conditions used to obtain kinetic data were 750-850°C and an O<sub>2</sub> pressure of 100 Torr. In order to obtain information on change in dimensions of the samples upon oxidation at conditions comparable to those used to study the reaction of oriented pyrolytic graphite[7], glassy carbon samples were also reacted at 900°C and an O<sub>2</sub> pressure of 30 Torr.

Adsorption measurements were attempted, using the same reaction system and CO<sub>2</sub> or Ar at 195°K and 77°K, respectively.

## 3. RESULTS

Typical plots of oxidation rates vs time for various samples and temperatures are shown in Fig. 1. In every case there is an initial high reaction rate which drops to a constant value, the time taken to reach a constant value decreasing with increasing reaction temperature. In all cases, attainment of a steady state rate occurs at a burn-off ranging from 7 to 10 per cent. Experimental runs were discontinued either after about 20 hr, when the oxidation rate had remained constant for a long period of time as was the case for the lower temperature runs, or after noting a decrease in the steady state rate for runs at higher temperatures (800 to 850°C). An Arrhenius plot of the steady state rates, taken from Fig. 1, gave a good straight line with a slope of  $63 \pm 3$  kcal/mole.

Once the reaction rate began decreasing following the steady state period it continued to do so up to very high values of burn-off. For example, at 800°C the reaction rate began to decrease at about 11 per cent burn-off from a

\*Present Address: Department of Inorganic Chemistry, University of Granada, Spain.

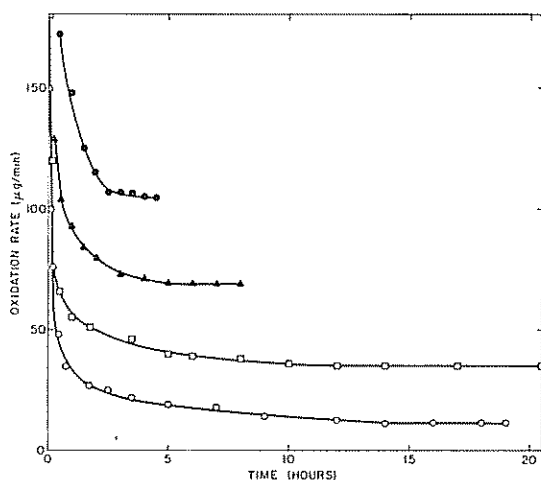


Fig. 1. Change of reaction rates with reaction time for oxidation of glassy carbon at: ● 850°C, ▲ 800°C, □ 775°C, and ○ 750°C.

value of 69  $\mu\text{g}/\text{min}$  to a value of 23  $\mu\text{g}/\text{min}$  at 80 per cent burn-off. The decrease in rate, as a function of burn-off, was linear and was much less marked than the initial sharp fall-off in rate in the early stages of a run.

Changes in thickness of a sample were monitored after a number of incremental burn-offs at 900°C, the results being shown in Fig. 2. A plot of percentage thickness decrease vs percentage burn-off presents two distinct regions. Up to about 40 per cent burn-off, results fall on a straight line having a slope less than one, indicating some internal burning. Above about 50 per cent burn-off, results also fall on a straight line but with a slope close to one. These measurements were made at the center of the sample plate. After 40 per cent burn-off, measurements

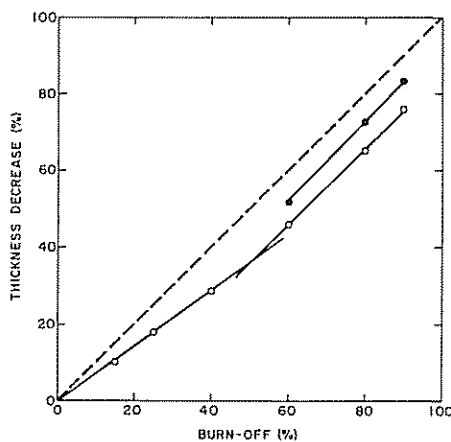


Fig. 2. Change in sample thickness with oxidation at 900°C for measurements at: ○ center of plate and ● edge of plate. Dashed line represents equality of percentage of thickness decrease with percentage burn-off increase.

were also taken at the edges of the plate. Here again decrease in thickness with burn-off can be expressed by a straight line of slope one. However, for fixed values of burn-off between 60–90 per cent, decrease in sample thickness is greater at the edge than at the center of the plate.

For five samples which had undergone about 40 per cent burn-off, it was attempted to measure adsorption of Ar at 77°K (up to a relative pressure of 0.5) and CO<sub>2</sub> at 195°K (up to a relative pressure of 0.2). No detectable weight increase could be measured by the microbalance, indicating (from the sensitivity of the balance) that the specific surface area of the samples was at least less than 1 m<sup>2</sup>/g.

Changes in dimensions of glassy carbon samples were also monitored as oxidation proceeded at 900°C and 30 Torr O<sub>2</sub> pressure. A sample was taken up to 80 per cent burn-off in four steps and the dimensions measured after each step. Results, plotted in Fig. 3, show recession in directions both perpendicular and parallel to the glassy carbon plate as a function of time. Also shown in Fig. 3 are results for plates of pyrolytic carbon APG142. The structure of this sample is discussed in detail elsewhere[7]. Both carbon samples had a starting thickness of essentially 1 mm. The planar dimensions, on a side, were 10.5 and 12.8 mm for the glassy carbon and pyrolytic carbon, respectively. At the end of the runs, given by the last data point on each curve, both carbons had undergone approximately 80 per cent burn-off. Recession vs reaction time plots yield straight lines in each case but all plots do not go through the origin.

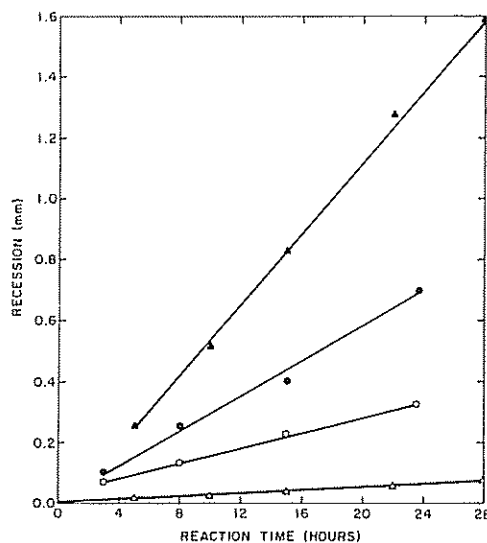


Fig. 3. Recession of plate samples vs reaction time at 900°C for oxidation to 80 per cent burn-off of: ○● glassy carbon and △▲ pyrolytic carbon. Open and closed symbols represent directions perpendicular and parallel to the plate surface respectively.

Recession rates for the glassy carbon in the directions parallel and perpendicular to the plate, calculated from the slope of the straight lines, are 0.029 and 0.012 mm/hr, giving an anisotropy ratio for reactivity of 2.4. Recession rates for the pyrolytic carbon in the directions parallel and perpendicular to the plate are 0.058 and 0.0026 mm/hr, giving an anisotropy ratio of 22.4.

#### 4. DISCUSSION

It is well to review briefly what is known about the physical structure of GC-30 glassy carbon. The material has an apparent density of 1.46 g/cc and an X-ray density of 2.22 g/cc, giving a porosity of 0.235 cc/g or 34 per cent. This porosity is closed to helium, even at high temperatures. From Raman spectroscopy studies it is concluded that the bonding is primarily trigonal, as in graphite[8]. From small angle X-ray scattering studies, using a treatment of the data proposed by Perret and Ruland[9], the material is calculated to have a range of inhomogeneity,  $l_p$ , of 18A and a specific surface area of 350 m<sup>2</sup>/g[10]. From magnetic susceptibility studies a slight alignment of crystallites with their basal planes parallel to the surface of the glassy carbon plate was detected[11]. That is, with the magnetic field parallel to the plate surface,  $\chi_{\perp}$  was  $-5.18 \times 10^{-6}$ /g. With the magnetic field parallel to the plate surface,  $\chi_{\parallel}$  was  $-4.99 \times 10^{-6}$ /g. Using the relationship between  $\chi$  and average crystallite diameter suggested by Pinnick[12],  $L_n$  is estimated as 90A. From X-ray diffraction line broadening,  $L_r$  was estimated as 67A[11].

In light of the properties of GC-30 it is interesting to consider results on rates of surface recession during oxidation, as given in Fig. 3. As expected, recession rates of the glassy carbon, both parallel and perpendicular to the plate surface, are bracketed by recession rates for the highly oriented pyrolytic graphite sample.\* That is, reactivity of a trigonally bonded carbon crystallite is highly anisotropic; the oxidation rate perpendicular to the basal plane is much less than that parallel to the basal plane[14]. Thus pyrolytic graphite sample APG142, with a mosaic spread of only about 4.0° from the plate surface[7], would be expected to show the lowest recession rate upon oxidation perpendicular to the plate

surface and the highest recession rate parallel to the plate surface. As expected the ratio of recession rates in the two directions has been shown to increase as the mosaic spread increases[7].

The slight anisotropy shown for the recession rates of glassy carbon can be attributed to at least two factors. First, magnetic susceptibility data show slight preferential crystallite alignment. Second, it is expected that carbon atoms located along the intersections of the sample surfaces will have the highest reactivity. Indeed, it was noted in Fig. 2 that the glassy carbon plate decreased in thickness more rapidly at its edge than at its center. Since the fraction of carbon atoms located along intersections to the total number of surface carbon atoms is higher in the edge surface of the sample than in the top and bottom plate surfaces, this would result in a greater recession rate in the edge surface.

When comparing the oxidation of glassy carbon and stress recrystallized pyrolytic graphite, the sample shape of the pyrolytic graphite will be a major factor in determining which sample has the over-all higher oxidation rate. In the present case with samples of close to the same shape, the over-all oxidation rate of GC-30 at 900°C exceeds that of APG142. That is, oxidation of GC-30 to 80 per cent burn-off required 23.6 hr whereas a similar degree of oxidation of APG142 required 28 hr. Upon increasing the thickness to plate dimension ratio of APG142, a point would be reached where its consumption rate would equal and then exceed that of GC-30.

It is reported that GC-30 has an oxidation rate at 800°C which is one-third that of electrode graphite[15]. On the basis of these results, it is suggested that its lower oxidation rate can be attributed to its having a lower specific surface area. That is, the original surface area of GC-30 is essentially its geometric area, which would be of the order 10–20 cm<sup>2</sup>/g. Upon oxidation, it has been shown in this study, from gas adsorption measurements, that the specific area remains low, certainly less than 1 m<sup>2</sup>/g. On the other hand, electrode graphites have an original specific surface area of the order of 0.4 m<sup>2</sup>/g; and upon oxidation, the specific area increases to at least 2 m<sup>2</sup>/g[16]. Indeed on the basis of specific surface areas, it might be expected that there would be a greater difference in reactivity than a factor of three between GC-30 and electrode graphite. That there is not might be due to a difference in average shape of the crystallites in glassy and electrode carbons. That is, measurements just described on glassy carbon indicate that the  $L_n$  and  $L_r$  dimensions are essentially comparable. On the other hand, for electrode graphite the  $L_n/L_r$  ratio is reported to considerably exceed one[17]. Thus there would be a higher planar to edge surface ratio for the average electrode graphite crystallite than there would be for the average glassy carbon crystallite. This factor taken alone

\*It is well to keep in mind that the two carbons being considered have each been taken to temperatures around 3000°C. Thus their impurity contents are low and the catalytic effect on oxidation rates is expected to be small. On the other hand, if impurity content is significant, the effect of impurities on oxidation rates can override geometric effects which are discussed here. For example, the oxidation rate of Tokai glassy carbon heated to 2000°C (GC-20) is about 50 times higher[13] than that of the 3000°C material (GC-30). Heat-treatment between 2000 and 3000°C has resulted in a large decrease in ash content[13].

would result in a lower oxidation rate for the electrode graphite, as is implied from results in Fig. 3.

Overall, the oxidation behavior of glassy carbon, expressed as weight loss per unit reaction time, can be divided into three regimes. For low burn-offs, up to about 5 per cent, the oxidation rate decreases rapidly with increasing burn-off. There is next a limited regime of constant reaction rate, followed by an extended regime where rate falls off slowly and essentially linearly with additional burn-off, at least up to 80 per cent. It was previously reported that the oxidation rate of highly oriented pyrolytic graphite also decreases rapidly in the low burn-off regime [6]. A high initial rate in this case was attributed to the presence of loose and distorted material resulting from the initial cutting and polishing operation. In the case of the glassy carbon, where samples were simply broken off, it would seem that this could not be the explanation.

In another sense, these results show that glassy carbon is indeed a unique material. From small angle X-ray scattering and density measurements, it is known that glassy carbon has a large porosity existing in small voids. A closed surface surface area of  $350 \text{ m}^2/\text{g}$  is estimated. Yet, oxidation to large burn-offs does not result in the production of a large accessible surface area. This is in direct contrast to the behavior of other organic raw materials of small crystallite size, like coals, which also have large surface areas inaccessible to small molecules [18]. Activation in  $\text{O}_2$  or air results in large increases in available surface area up to values exceeding  $1000 \text{ m}^2/\text{g}$ . The difference in behavior of these materials appears to be due to structural differences. Glassy carbon lacks a macro or transitional pore system through which the oxidizing gas can diffuse relatively rapidly to the center of the particle. Thus oxidation of glassy carbon results primarily in consumption of carbon from the

surface, or close equivalence of volume change and weight change, as seen in Fig. 2. For carbonaceous solids which are good precursors for the production of activated carbon, oxidation and weight loss are generally accompanied by a minor decrease in particle size. That is, oxidation occurs primarily at internal surfaces.

#### REFERENCES

1. Lewis J. C., Redfern B. and Cowlard F. C., *Solid-State Electron.* **6**, 251 (1963).
2. Cowlard F. C. and Lewis J. C., *J. Mater. Sci.* **2**, 507 (1967).
3. Lewis J. C., *2nd Conf. Industr. Carbon Graphite*. Society of Chemical Industry, London, 1966, p. 258.
4. Higgins J. K., Discussion to Paper by Lewis J. C., *2nd Conf. Industr. Carbon Graphite*. Society of Chemical Industry, London, 1966, p. 268.
5. Noda T., Inagaki M. and Yamada S., *J. Non-crystalline Solids* **1**, 285 (1969).
6. Rodriguez-Reinoso F., Thrower P. A. and Walker P. L. Jr., *Carbon* **12**, 63 (1974).
7. Rellick G. S., Thrower P. A. and Walker P. L. Jr., *Carbon* **13**, 71 (1975).
8. Nakamizo M., Kammereck R. and Walker P. L. Jr., *Carbon*, **12**, 259 (1974).
9. Perret R. and Ruland W., *J. Appl. Cryst.* **5**, 183 (1972).
10. Jenkins R. G. and Walker P. L. Jr., *Eleventh Biennial Conf. Carbon*, Extended Abstracts, 1973, p. 182.
11. Mulay L. N. and Walker P. L. Jr., ARPA Report on *Glassy Carbon, Alloys*. Pennsylvania State University, January, 1972.
12. Pinnick H. T., *Phys. Rev.* **94**, 319 (1954).
13. Tingey G., ARPA Report on *Investigation of the Influence of Structure on Chemical Stability and Thermal/Mechanical Shock Properties of Glass-Like Carbon*. Battelle Northwest Laboratories, November, 1971.
14. Hennig G. R., *Chemistry and Physics of Carbon*, Vol. 2. Marcel Dekker, New York, 1966, p. 1.
15. Yamada S., *DCIC Report* 68-2. Battelle Memorial Institute, 1968, p. 12.
16. Walker P. L. Jr. and Raats E., *J. Phys. Chem.* **60**, 364 (1956).
17. Richards B. P., *J. Appl. Cryst.* **1**, 35 (1968).
18. Walker P. L. Jr. and Kini K. A., *Fuel* **44**, 453 (1965).