values of magnetoresistance, i.e. the same degree of graphitisation. One should consider two factors in analyzing the results shown in Fig. 3; first, the geometrical density effects such as effective cross-section and contact area between grains or particles, which have been discussed in detail by Mrozowski[4], and secondly the intrinsic resistivity components representing the difference in graphitisation.

The dotted line connecting the four solid points should correspond to purely geometrical density
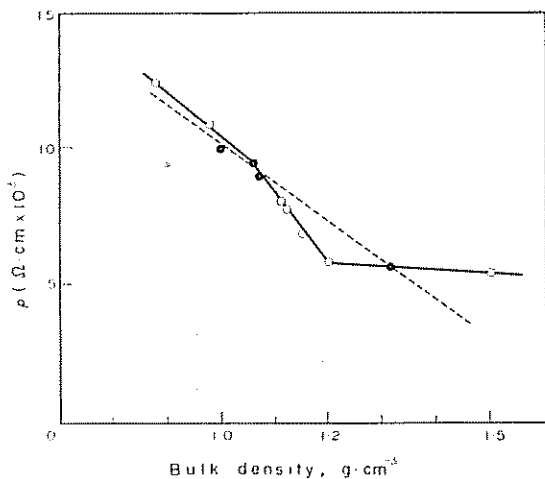

Fig. 3. Electrical resistivity as a function of bulk density of porous glassy carbons.

influence on the resistivity, because the degree of graphitisation is believed to be the same for these

samples, thus the second effect not being present. When the degree of graphitisation increases, the electrical resistivity decreases more rapidly with bulk density than the dotted line as can be seen in the density range up to $1 \cdot 2$ g·cm^{-3}, viz., the resistivity is depressed by the progressing partial graphitisation in addition to the geometrical density effect. Later, in the density range between $1 \cdot 2$ g·cm^{-3} and $1 \cdot 5$ g·cm^{-3}, with diminishing partial graphitisation, the resistivity decreases more slowly than the dotted line. Thus, the interpretation deduced from the magnetoresistance data concerning the partial graphitisation in porous glassy carbons, is consistent with the behavior of the electrical resistivity shown in Fig. 3.

K. KAWAMURA
T. TSUZUKU

College of Science and Engineering
Nihon University, Kanda-Surugadai
Chiyoda-Ku
Tokyo, Japan

REFERENCES

1. Yamaguchi T., *Carbon* 1, 47 (1963).
2. Kawamura K. and Jenkins G. M., *Proceedings of the 3rd Conference on Industrial Carbon and Graphite*, London. Soc. Chem. Ind., London, p. 98 (1970).
3. Franklin R. E., *Proc. Roy. Soc.*, London A 209, 196 (1951).
4. Mrozowski S., *Proceedings of the 1st and 2nd Conferences on Carbon*, Buffalo. The Waverly Press, Inc. p. 195 (1956).

Influence of Hydrogen Chemisorption on the Subsequent Chemisorption of Oxygen on Activated Graphon

It is well known that the chemical reactivity of carbons and graphites is profoundly influenced by the presence of surface oxygen and surface hydrogen groups attached to some of the peripheral carbon atoms of the layer planes. The quantity and the nature of such surface contaminants are largely dependent on the raw material selected for preparing the carbon, but the chemical reactivity is undoubtedly a function of the amount of the surface contaminant and the number of chemical groups at edge carbon atoms. For example, Bangham and Stafford[1], while studying kinetics of the

disappearance of oxygen on Acheson graphite, observed that the adsorption of hydrogen enhanced the adsorption of oxygen. They suggested that hydrogen forms ethylenic linkages and the oxygen atoms tend to add themselves to pairs of unsaturated carbon atoms. Barrer[2] studied the interaction of hydrogen with oxide-covered carbon surfaces and observed that oxygen acts as a poison for the adsorption of hydrogen. Thomas[3] also observed that oxygen adsorbed on reactor grade graphite blocks sites capable of adsorbing hydrogen.

The present authors have carried out extensive studies on the chemisorption of oxygen and hydrogen, separately, on cleaned Graphon surfaces[4-6]. It was concluded that the chemisorption of oxygen and hydrogen takes place on the same set of active sites, although the

level of activation energies associated with hydrogen chemisorption is larger than that for oxygen chemisorption.

It is known that the carbon–hydrogen surface complex is much more stable than the carbon–oxygen surface complex[7, 8, 9]. It may be worthwhile to block the active sites with hydrogen and thus effect a considerable decrease in the subsequent chemisorption of oxygen. As the chemisorption of oxygen is a prerequisite to carbon gasification, contamination of carbons with hydrogen may be useful in reducing, to some extent, the gasification of carbon materials. Further, it has been shown that the chemisorption of oxygen on carbon changes sites from being hydrophobic to hydrophilic[10]. Thus, chemisorption of hydrogen might be expected to maintain the carbon surface in a hydrophobic state.

It was thought of interest, therefore, to contaminate the cleaned Graphon surface with different amounts of hydrogen and then to study the chemisorption of oxygen over the contaminated surface. In a few experiments, the cleaned Graphon surface was first contaminated with oxygen and then the chemisorption of hydrogen was studied. The apparatus and techniques used to study chemisorption of gases on Graphon have been described in detail[4, 5, 6]. Identical techniques were used in this study. The sample of Graphon used had previously been burned off to 16·6 per cent to introduce significant active surface area[11].

Oxygen adsorbed as a function of time on the cleaned Graphon surface and on the Graphon surface deliberately contaminated with different amounts of hydrogen is shown in Fig. 1. The

hydrogen was chemisorbed at 300°C in runs (2) and (3) and 500°C in run (4). In each case, hydrogen adsorption times were sufficiently long for essentially equilibrium hydrogen preadsorption coverage to be achieved. As shown previously[6], the extent of this coverage is a function of hydrogen pressure as well as temperature. In runs (2) and (4), a hydrogen pressure of 105 millitorr was used; in run (3), the pressure was 225 millitorr.

The presence of hydrogen considerably reduces the chemisorption of oxygen. For example, when $2·6 \times 10^{18}$ atoms of hydrogen per gram of Graphon were chemisorbed, oxygen uptake, in 400 min, was reduced from $10·6 \times 10^{18}$ to $6·5 \times 10^{18}$ atoms of oxygen per gram of Graphon. At 400 min the chemisorption rate was small. In Fig. 2 the amount of oxygen adsorbed as a function of amount of hydrogen preadsorbed is plotted for different adsorption times. It is interesting that the plots are not linear, with one atom of hydrogen preadsorbed resulting in a decrease in chemisorption of one atom of oxygen. Rather, for low hydrogen coverages each atom of hydrogen chemisorbed results in a reduction of more than one atom of oxygen chemisorbed, it being close to two oxygen atoms per hydrogen atom. On the other hand, for large amounts of hydrogen chemisorbed further reduction in oxygen chemisorption is small.

In the case of oxygen chemisorption, it has been shown conclusively that adsorption is dissociative, with one oxygen atom occupying one carbon atom in the prismatic surface[10, 12]. The activated complex leading to chemisorption would be expected to be formed by two oxygen atoms and two surface carbon atoms. Preadsorption of hydrogen
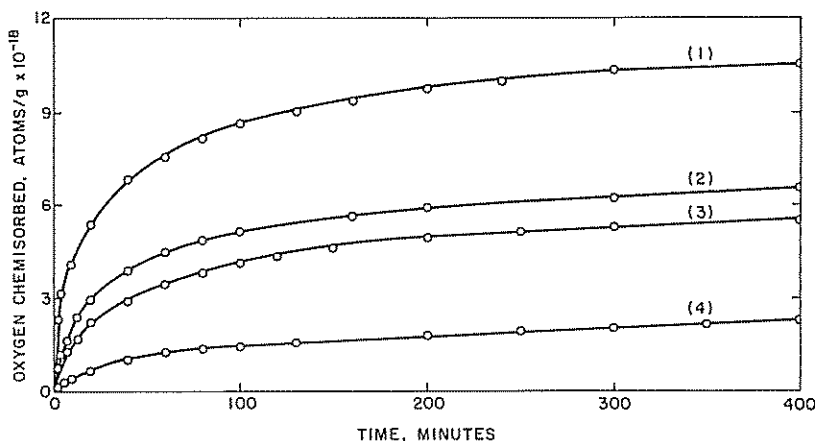

Fig. 1. Effect of hydrogen chemisorption on the subsequent chemisorption of oxygen on 16·6 per cent burn-off Graphon. Oxygen chemisorption at an oxygen pressure of 100 millitorr and 100°C. Hydrogen prechemisorbed in atoms/g: Curve (1), nil; (2), $2·6 \times 10^{18}$ (3), $5·2 \times 10^{18}$ (4) $10·5 \times 10^{18}$.
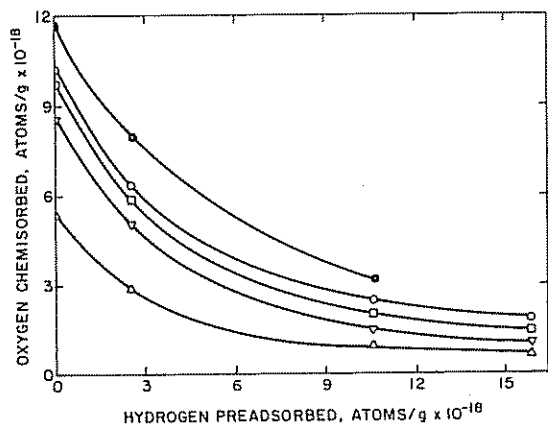
Fig. 2. Relationship between amount of hydrogen prechemisorbed and subsequent oxygen chemisorption (oxygen pressure of 100 millitorr and 100°C) for selected adsorption times: △, 20 min; ▽, 100 min; □, 200 min; ○, 300 min; ◉, 24 hr.

Table 1. Effect of hydrogen preadsorption on the subsequent rates of oxygen chemisorption at selected times

Hydrogen adsorbed (atoms/g $\times 10^{-18}$)	Rate of oxygen chemisorption (atoms/g/min $\times 10^{-18}$) after	
	40 min	100 min
nil	0·132	0·054
2·6	0·084	0·042
5·2	0·072	0·036
10·5	0·036	0·030

would decrease the concentration of adjacent unoccupied surface carbon sites; and it would be expected that one hydrogen atom would result in a decrease in chemisorption of more than one oxygen atom. The fact that at larger amounts of hydrogen chemisorbed, one hydrogen atom adsorbed results in only a fractional decrease in oxygen atom adsorption can have a number of explanations. First instead of just one hydrogen atom adsorbing on one carbon site, two hydrogen atoms could adsorb on some of the edge carbon sites, as suggested by Long and Sykes[13]. Second, oxygen could be adsorbing on some edge carbon sites which are not active for hydrogen chemisorption. Third, oxygen adsorption on some sites could be enhanced by prior hydrogen chemisorption as suggested by Bangham and Stafford[1].

The rates of oxygen adsorption on the cleaned Graphon surface and on the Graphon surface contaminated with hydrogen (as calculated by drawing tangents to the plots in Fig. 1) at two different times are shown in Table 1. There is a continuous decrease in rate of oxygen chemisorption with increasing amounts of hydrogen preadsorbed.

In another experiment oxygen was first chemisorbed on the cleaned Graphon surface at 100°C followed by chemisorption of hydrogen at 300°C using a hydrogen pressure of 105 millitorr. The chemisorption of as little as $1·2 \times 10^{18}$ atoms of oxygen/g. resulted in a decrease of hydrogen chemisorption from $2·8 \times 10^{18}$ to $0·82 \times 10^{18}$ atoms/g. Thus, in this case the decrease in hydrogen adsorption was also greater than the amount of oxygen preadsorbed at this low oxygen

coverage. Each oxygen atom chemisorbed resulted in the reduction in chemisorption of almost two hydrogen atoms.

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R. C. BANSAL
F. J. VASTOLA
P. L. WALKER, JR.
Department of Material Sciences
Pennsylvania State University
University Park, Pennsylvania 16802, *U.S.A.*

REFERENCES

1. Bangham D. H. and Stafford J., *J. Chem. Soc.* **127**, 1085 (1925).
2. Barrer R. M., *J. Chem. Soc.* 1261 (1936).
3. Thomas W. J., *J. Chim. Phys.* **57**, 61 (1960).
4. Walker, P. L. Jr., Bansal R. C. and Vastola F. J., *The Structure and Chemistry of Solid Surfaces* John Wiley and Sons, New York, 1969, pp. 81–1 to 81–16.
5. Bansal R. C., Vastola F. J. and Walker P. L. Jr., *J. Colloid Interface Sci.* **32**, 187 (1970).
6. Bansal R. C., Vastola F. J. and Walker P. L. Jr., *Carbon* **9**, 185 (1971).
7. Redmond J. P. and Walker P. L. Jr., *J. Phys. Chem.* **64**, 1093 (1960).
8. Phillips Roger, Vastola F. J. and Walker, P. L. Jr., *Carbon* **8**, 197 (1970).
9. Bansal R. C., Vastola F. J. and Walker P. L. Jr., *Carbon* **8**, 443 (1970).
10. Walker P. L., Jr. and Janov Juri, *J. Colloid Interface Sci.* **28**, 449 (1968).
11. Laine N. R., Vastola F. J. and Walker P. L. Jr., *J. Phys. Chem.* **67**, 2030 (1963).
12. Walker P. L. Jr., Austin L. G. and Tietjen J. J., *Chemistry and Physics of Carbon*, P. L. Walker, Jr., Editor. Marcel Dekker, New York, Vol. 1, 1966, pp. 327–365.
13. Long F. J. and Sykes K. W., *Proc. Roy. Soc.* **A193**, 377 (1948).

Chemical Vapour Deposition of Pyro-Carbon, SiC, TiC, TiN, Si and Ta on Different Types of Carbon Fibres

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The application of carbon fibres for reinforcement of composites is limited because of the chemical reactivity between carbon and most of the nonpolymeric matrix materials. The coating of fibres has been found to be a suitable way to avoid this disadvantage, as well as to improve the adherance between fibre and matrix[1–4].

This letter is concerned with experimental results concerning the influence of CVD-coatings on the mechanical properties of carbon fibres. The deposition of SiC and TiC was performed to obtain a barrier against carbon diffusion. Ta, TiN and Si coatings are promising wetting promotors for metals, while pyro-carbon as coating on the fibres is of interest in carbon–carbon composites. Commercial types of carbon fibres were used, such as WYB, Thornel 25, 50 and 75 which are produced from cellulose-precursor and have a profiled surface, as well as Modmor IV and a laboratory fibre product, both made from PAN-precursors with a circular cross section of monofilaments.

The mechanical properties are listed in Table 1. The coatings were deposited from the vapours of chlorides of Ta and Ti, chloro- and methylchlorsilanes as well as methane in hydrogen and nitrogen atmosphere. Table 2 gives a survey of the main temperature and pressure conditions as well as residence times for obtaining coating thicknesses between 0·1 and 1 μm. All experiments were performed under steady state conditions in a tubular reactor with a hot wall arrangement shown in Fig. 1.

The apparatus consisted of a graphite tube 40 cm long heated by induction and a device for the fibre transport between both ends of the reactor. The whole apparatus is surrounded by a quartz glass shell which permits a controlled supply and removal of the reaction gases. Carbon fibre-bundles with a total length of up to several hundred metres have been continuously coated. Carbon fibre-yarns consisting of several thousand monofilaments are geometrically complicated porous bodies. As the coating of all monofilaments within the yarn with uniform layer thickness has to be performed simultaneously, the deposition rate must be controlled by the chemical reaction, and not by the diffusion rate of the gases to the fibre surface. If this condition is not achieved, the outer monofilaments of the yarns would be preferrably coated and also bridges would be formed between the different filaments. The monofilaments of most commercial carbon fibres have thicknesses between 5 and 9 μm. As the spaces between the monofilaments in the yarn during coating vary between a fraction of a micron and several microns the maximum coating thickness is limited up to 1 μm. Additionally, the yarns are differently treated. As shown in Figs. 2 and 3 with the examples pyro-carbon and TiN, uniform coating thicknesses of 0·2 μm as well as 0·8 μm were achieved on each monofilament within the bundle.

Table 1

	Ultimate tensile strength (kP/mm^2)	Young's modulus (kP/mm^2)	Elongation at break (%)	Average fibre diameter (μm)
WYB*	50–64	3800–4200	1·5–1·6	8·9
Thornel/25*	120–130	15000–17000	0·6–0·9	7·4
Thornel 150*	140–170	28000–30000	0·5–0·7	6·6
Thornel 75*	240–260	45000–50000	0·5–0·6	5·8
Modmor Type IV†	130–190	26000–28000	0·5–0·7	7–8
Lab. fibre‡ Product	80–140	ca. 16000	0·9	ca. 9

*UCC/USA.
†Morganite/England.
‡Inst. für Chemische Technik der Universität Karlsruhe.