# Reorientation Effects in Vitreous Carbon and Pyrolytic Graphite

J. C. LEWIS, I. J. FLOYD

*Allen Clark Research Centre, The Plessey Co Ltd, Caswell, Towcester, Northants, U K*

Tubular specimens of vitreous carbon and of pyrolytic graphite, heated in nitrogen or helium for several minutes at 2850 to 3100° K by RF induction, developed a "skin" of crystalline carbon, nodular in appearance and apparently growing *into* the carbon from the surface. The vitreous carbon was isotropic, with no preferred orientation of "crystallites"; the pyrolytic graphite had a preferred orientation of basal planes at right angles to the axis of the specimen, so that curved surfaces were composed predominantly of edge atoms. X-ray diffraction studies of the skin indicated that it was partially graphitised and strongly orientated with basal planes parallel to the surface. The mechanism of the reorientation process is as yet not clear, but the driving force may be a change in surface free energy.

## 1. Experimental
### 1.1. Heat Treatment Procedure
As part of a research project on the gaseous oxidation of various carbons at high temperatures, a series of preheating experiments was carried out in order to determine to what extent the reactivity of a specimen was dependent upon its immediate thermal history. The apparatus used (fig. 1) was designed for the oxidation studies, and consisted of a steel pressure vessel fitted with facilities for heating small carbon specimens by RF induction in a stream of gas; the temperature of the inside surface of the specimen was measured by means of a recording optical pyrometer, coupled to a millivolt recorder. Tubular specimens, 1.5 cm long × 1.6 cm inner diameter × 2.0 cm outer diameter, were made in three materials: Plessey vitreous carbon, prepared in these laboratories by the pyrolysis of phenolic resins; pyrolytic graphite (from Supertemp Corp, deposition temperature about 2300° K) having the *c* axis parallel to the axis of the specimen; and Le Carbone P5890 graphite (a close-grained synthetic graphite). Each specimen was mounted in a sheath (fig. 2a) of Morganite EY9 graphite, which was set up in the reaction vessel as shown in fig. 1. The vessel was evacuated and then filled with either nitrogen (Air Products Ultra-Pure, dew-point 189° C, $O_2$ 4 ppm) or helium (British Oxygen
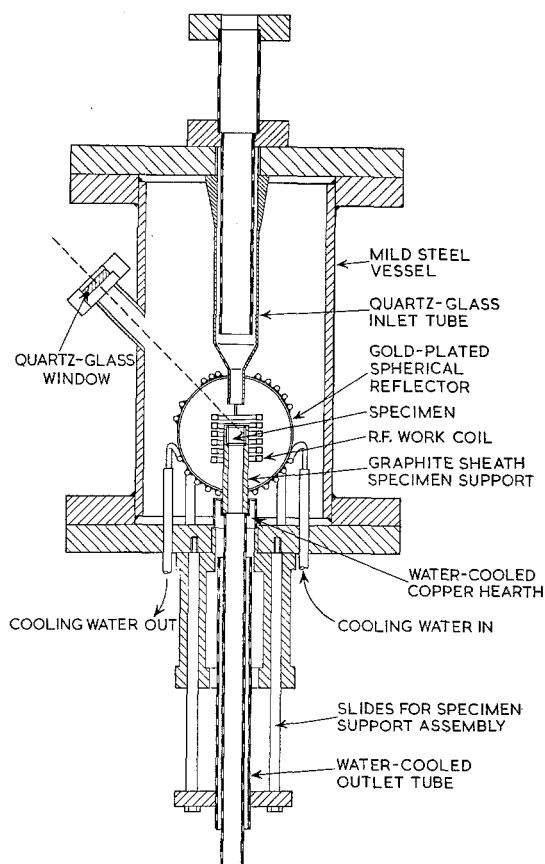


*Figure 1* Reaction vessel.

Labels: MILD STEEL VESSEL; QUARTZ-GLASS INLET TUBE; GOLD-PLATED SPHERICAL REFLECTOR; SPECIMEN; R.F. WORK COIL; GRAPHITE SHEATH SPECIMEN SUPPORT; QUARTZ-GLASS WINDOW; WATER-COOLED COPPER HEARTH; COOLING WATER OUT; COOLING WATER IN; SLIDES FOR SPECIMEN SUPPORT ASSEMBLY; WATER-COOLED OUTLET TUBE
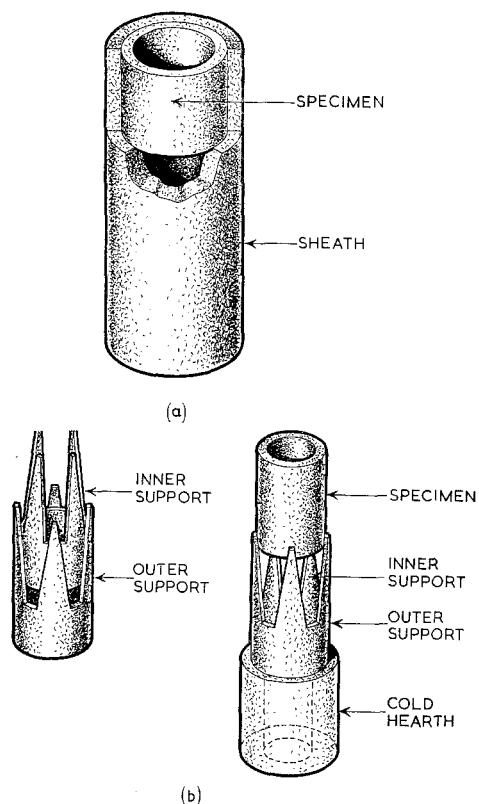
Figure 2 Specimen supports: (a) sheath type; (b) "crown" type.

Co, main impurity 0.2% nitrogen). The specimen and sheath were then heated to a temperature in the range 2850 to 3100° K for several minutes, in a stream of nitrogen or in static helium, and allowed to cool in the same atmosphere. Removal of a vitreous carbon specimen for examination after heating in nitrogen showed that a flaky "skin" had formed both inside and outside the specimen; fragments of the skin were examined under a low-power microscope, and it was found that the original surface and the underlying surface of the specimen were not significantly changed, but that the inside of the skin was nodular in appearance. Repetition of the experiment with pyrolytic graphite specimens yielded similar results except that the skin was less flaky and more coherent; on one occasion a complete cylindrical shell, approximately 0.5 mm thick, was formed on the outer surface of the specimen. It was removed in one piece by slitting down one side with a razor blade and sliding the split shell off the specimen. Repeated attempts to produce similar skins on the P 5890 graphite were unsuccessful, although

a few scattered globules, probably of deposited carbon, were visible on the surface after treatment.

In order to determine whether a reaction with nitrogen (e.g. formation and decomposition of cyanogen) was responsible for the effect, the work was repeated, with similar results, in helium containing only 0.2% nitrogen; the rate of growth of skin was approximately the same as in nitrogen, suggesting that the latter was not playing a significant part in the process (unless the reaction were of zero order, which was considered unlikely). Argon, which was readily available in a much purer state, could not be used because of rather violent RF discharges which caused large power losses and appreciable volatilisation of sheath or specimen material. The possible influence of the graphite sheath was eliminated as far as possible in a further short series of experiments with an alternative form of specimen support ("crown" type, fig. 2b) in which the contact area between the specimen and the EY 9 graphite was reduced to a few square mm. There was a tendency for the skin to develop from the lower end of the specimen, i.e. the end in contact with the EY9, suggesting that the latter may act as a nucleating agent.

Visual examination of specimens after heat treatment suggested that the source of carbon for the formation of the skin was the specimen itself and not the graphite support; this was confirmed by weighing, the weight of the skin being only a few mg less than the weight loss of original material.

The density of the skin material, determined by the "sink or float" method using bromoform/ethanol mixtures, was $2.15 \pm 0.02$ g/cm$^3$ for both start materials. This is almost as high as that of the pyrolytic graphite (2.21) and much higher than that of the vitreous carbon (1.46).

## 1.2. Microscopic Examination

In all cases, skins developed on vitreous carbon or pyrolytic graphite specimens (fig. 3) presented a nodular appearance on their inside surface. More detailed examination of vitreous carbon skins revealed that their outside surface, i.e. the original surface of the specimen, was also covered with very much smaller nodules. The nodular material appeared to have grown away from the original surface, or from an array of black specks ("soot" particles?) on or near the surface; the process being similar to that observed during the preparation of pyrolytic
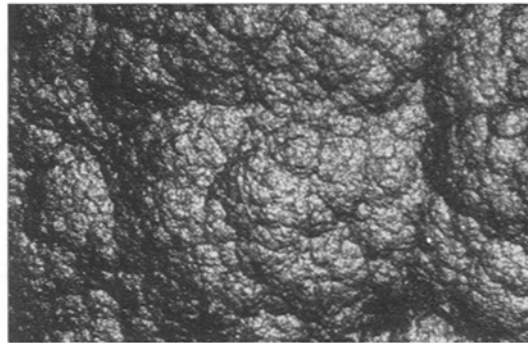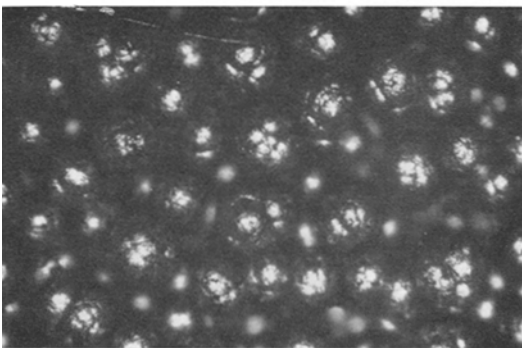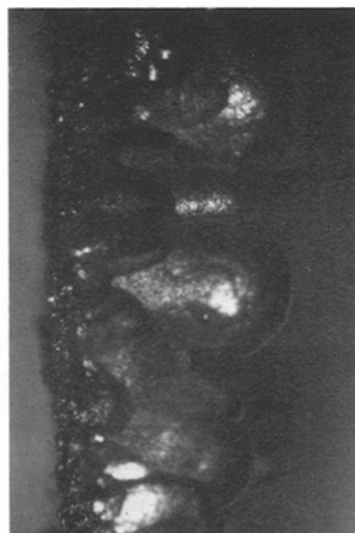
155

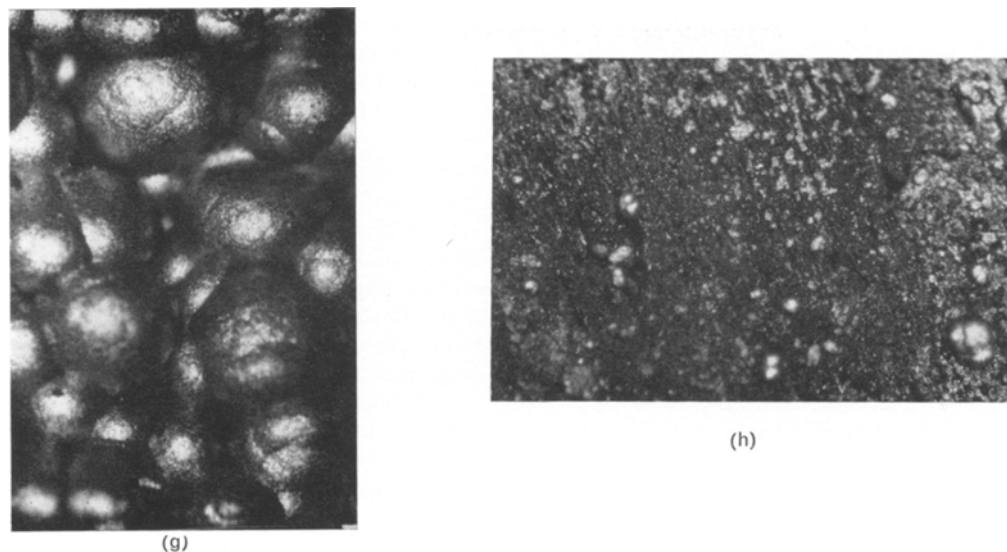(a)
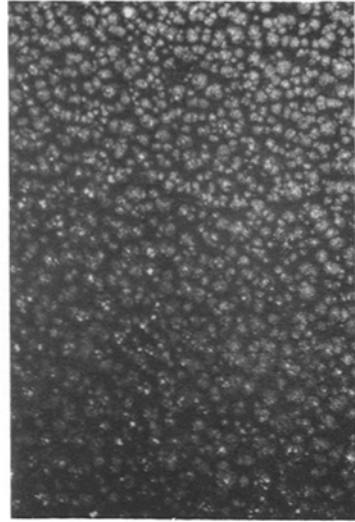


(d)
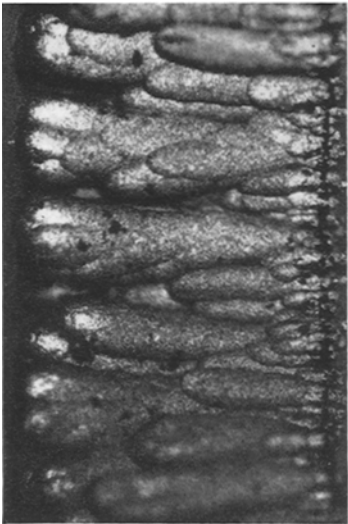


(b)



(e)



(c)



(f)

*Figure 3* Photomicrographs ($\times$ 40): (a) Vitreous carbon before treatment: broken section (conchoidal fracture); (b) Skin from vitreous carbon after treatment: broken section; (c) Skin from vitreous carbon after treatment: inner surface; (d) Skin from vitreous carbon after treatment: outer surface; (e) Pyrolytic graphite before treatment: broken section (basal plane surface); (f) Skin from pyrolytic graphite after treatment: broken section; (g) Skin from pyrolytic graphite after treatment: inner surface; (h) Skin from pyrolytic graphite after treatment: outer surface.

graphite by the pyrolysis of hydrocarbon vapours on a heated substrate; the nodules increase in diameter, and decrease in number, with distance from the nucleation surface. The nodules formed on vitreous carbon were more elongated in shape than those on pyrolytic graphite.

## 1.3. X-ray Examination

X-ray diffraction examination of the products was carried out with a Guinier focusing camera using monochromatised radiation (Cu and Co). Intensities were measured on a Loebl recording microdensitometer. $L_a$ and $L_c$ were estimated by the method of Biscoe and Warren [1]; $p$, the probability that any two adjacent hexagonal layers will be misorientated, was estimated from the inter-layer spacing $C_o/2$ [2]. The results are tabulated below.

| Material | $L_a$ (Å) | $L_c$ (Å) | $C_o/2$ (Å) | $p$ |
|---|---|---|---|---|
| Vitreous carbon, substrate before treatment | 50 | 15 | | 1.0 |
| Vitreous carbon, nodular product | 350 | 150 | 3.38$_5$* | 0.6 |

| Material | $L_a$ (Å) | $L_c$ (Å) | $C_o/2$ (Å) | $p$ |
|---|---|---|---|---|
| Pyrolytic graphite, substrate before treatment | 360 | 520 | 3.42† | 0.9 |
| Pyrolytic graphite, substrate after treatment | 2000 | very large | 3.38† | 0.6 |
| Pyrolytic graphite, nodular product | 360 | 130 | 3.38* | 0.6 |

*From (00.4) peak
†From (00.2) peak, (00.4) too weak to measure because of preferred orientation.

The nodular skin showed a very strong preferred orientation with basal planes parallel to the surface, i.e. $c$ axis at right angles to the axis of the cylindrical specimen, for both start materials.

## 2. Discussion

The appearance of the product is somewhat similar to that of other well-orientated carbon deposits, e.g. those formed by the pyrolysis of methane [3] or by vacuum deposition [4].

157

The X-ray diffraction results indicate that the product is appreciably better ordered than the start materials, with a larger crystalline size and lower misorientation factor, although in the case of the pyrolytic graphite the substrate itself exhibits even more pronounced crystal growth as a result of the heat treatment than does the skin. The most significant conclusion from the results however is that both vitreous carbon and pyrolytic graphite appear to have undergone superficial reorientation, so that external surfaces, and particularly the interface with the EY9 graphite support, have become basal-plane surfaces. The structure of the skin is thus quite different from that of vitreous carbon, which is believed to consist of a completely random array of very small turbostratic "crystallites", with no true graphite orientation between adjacent layer planes in a "crystallite" and no preferred orientation of "crystallites" with respect to the surface; all bulk properties of vitreous carbon are therefore isotropic. For pyrolytic graphite specimens, the structure of the skin is similar to that of the start material, but the $c$ axis of the former is at right angles to that of the latter.

Qualitative spectrographic analysis of the skins and their respective start materials revealed only slight differences in impurity contents. The following elements were detected.
*Pyrolytic graphite*: Ca, Mg, Si, Cu, Al, Na. The skin also contained Fe and Ti (probably of the order of 10 ppm).
*Vitreous carbon*: Na, Ca, Mg, Si, Fe, K, Cu, Al. The start material also contained a slight trace of Ag.

Although the mechanism of the reorientation process is not yet clear, the driving force may be a thermodynamic one, resulting from the surface free energy of the basal plane being lower than that of a surface consisting partly or almost entirely of "edge" atoms (as in vitreous carbon and pyrolytic graphite of the orientation used, respectively). This suggestion is consistent with the tendency for carbon deposited from the vapour phase [3, 4] to orientate in the same way, and also for the similar effects observed in the graphitisation of certain carbon blacks [5]: such observations suggest that the basal-plane ($c$) surface of graphite is thermodynamically more stable than the edge-atom ($a$) surface, and carbon may therefore be expected to undergo surface reorientation, so as to expose $c$ rather than $a$

surfaces, whenever conditions are suitable. It is suggested that the main condition required is a high degree of mobility, either of single atoms or perhaps of aggregates of atoms (e.g. individual layer planes); this is likely to obtain both during deposition from the vapour phase at temperatures above about 2000° K and during very high temperature treatment of the type described here. It is to be expected that edge atoms, which are not so strongly bonded to the main structure as atoms nearer the centres of basal planes, will be more mobile and will evaporate more readily; this would explain why "microcrystalline" carbons, such as vitreous carbon and carbon blacks, and the $a$ surface of pyrolytic graphite, undergo reorientation more readily than a synthetic graphite such as the EY9 and P5890 graphites used in the present work, which have a comparatively large "crystallite" size (typical values for P5890 were $L_a \simeq$ 165 Å, $L_c \simeq 350$ Å, $p \simeq 0.35$) and consequently a smaller proportion of edge atoms.

An interesting result of the preference of surfaces to adopt a basal-plane orientation was noticed during examination of the complete cylindrical shell formed on a pyrolytic graphite specimen (fig. 4); the shell was found to be of
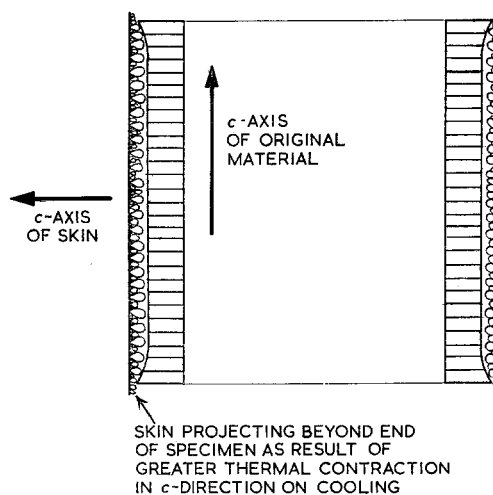


SKIN PROJECTING BEYOND END
OF SPECIMEN AS RESULT OF
GREATER THERMAL CONTRACTION
IN $c$-DIRECTION ON COOLING

*Figure* 4 Appearance of pyrolytic graphite specimen with external reorientated skin (vertical section).

more or less uniform thickness, about 0.5 mm, except near the ends, where if this skin thickness had been maintained a 0.5 mm ring of the original basal-plane surface on each end of the specimen would have had to be converted to the "edge" orientation. Instead, there was a dis-

continuity in the structure at each end as shown in fig. 4, so that the skin was tapered to zero thickness at the ends and the whole surface was maintained in the preferred orientation.

Two possible mechanisms for the process have been considered.

(a) *Solid phase recrystallisation* could occur by rearrangement of layer planes, as in the generally accepted mechanism for the graphitisation of carbons. The main objection to this mechanism is that the underlying surface of the specimen is never a replica of the inner surface of the skin, but appears virtually unchanged by the heat treatment, suggesting that there is a slight gap between the skin and the specimen throughout the reorientation process. In some experiments, moreover, the skin tended to adhere more strongly to the graphite sheath than to the specimen, and to follow the contours of file-cuts in the sheath, which was apparently acting as a nucleation surface.

(b) *Vapour phase transfer* Experiments such as that just mentioned suggest that the mechanism may involve an evaporation of loosely-bonded edge atoms followed by deposition on any convenient surface; provided that the heat evolved during deposition can be dissipated, the deposit (*c* surface) will have a lower vapour pressure than the original (random or *a*) surface and will therefore tend to act as a nucleation surface for further deposition rather than to re-evaporate. It is difficult to understand how such a process could occur in the absence of a sheath or on the inside of a specimen; however, it is possible that surface debris could act as nucleation centres for the formation of an initial thin film of deposited carbon adjacent to the surface (the black specks and external growth visible in figs. 3b and 3f?); this film would then tend to grow preferentially inwards simply because the carbon vapour concentration is higher than at the outer surface of the skin.

So far as is known, surface reorientation effects of the type described have not been observed during heat treatment of specimens of vitreous or pyrolytic carbon in graphite tube furnaces, at temperatures up to about 3000° K. Some attention was therefore given to the possibility that the RF induction heating technique was in some way responsible for the reorientation, e.g. by causing a radial temperature gradient near the surface or by promoting alignment of the basal planes in the direction of flow of current. However, temperature measurements with an optical pyrometer through small holes drilled in the specimen and sheath showed that temperature gradients were small (10 to 20° K across the specimen wall); and heat treatment of a "shell"-type pyrolytic graphite specimen (*a* axis circumferential) led to reorientation of the end (*a*) surface to give a thin *c* skin, i.e. the reverse process from that observed for the specimens previously used. Further work with other heating methods is desirable.

It has been suggested that the technique could be used for converting the more chemically reactive *a* surfaces of machined pyrolytic graphite shapes to *c* surfaces. However, there would be a major problem of expansion mismatch between the skin and the substrate because of the much lower coefficient of thermal expansion in the *a* than in the *c* direction.

## Acknowledgements

## References

1. J. BISCOE and B. E. WARREN, *J. Appl. Phys.* 13 (1942) 364.
2. R. E. FRANKLIN, *Acta Cryst.* 4 (1951) 253.
3. A. R. G. BROWN and W. WATT, "Industrial Carbon and Graphite", Proc. Conf. Soc. Chem. Ind. (London, 1957), p. 86.
4. D. E. PALIN, *Nature* 178 (1956) 809.
5. E. A. KMETKO, Proc. 1st Carbon Conf. (Buffalo, 1953; published 1956), p. 21; *Phys. Rev.* 86 (1951) 651.