

Fullerene-related structure of commercial glassy carbons

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ABSTRACT

Glassy carbon is a technologically important material widely used in products such as electrodes and high-temperature crucibles. However, the properties which make glassy carbon so valuable in these applications are poorly understood, since its detailed atomic structure is not known. A model for the structure of glassy carbon put forward many years ago has gained wide acceptance, but appears to suffer from serious shortcomings. In particular, it fails to account for the chemical inertness of the carbon, and for its high proportion of closed porosity. Here I show, using high-resolution transmission electron microscopy, that glassy carbons obtained from commercial suppliers contain a high proportion of fullerene-related structures. On the basis of these observations, models are put forward for the structures of ‘low-temperature’ and ‘high-temperature’ glassy carbons which incorporate non-six-membered rings.

§1. INTRODUCTION

Glassy carbon is an example of a non-graphitizing carbon, that is a carbon which cannot be transformed into crystalline graphite even at temperatures of 3000°C and above (Franklin 1951, Harris 1997). In addition to very high thermal stability, its distinguishing properties include its extreme resistance to chemical attack: it has been demonstrated that the rates of oxidation of glassy carbon in oxygen, carbon dioxide or water vapour are lower than those of any other carbon (Jenkins and Kawamura 1976). It is also highly resistant to attack by acids. Thus, while normal graphite is reduced to a powder by a mixture of concentrated sulphuric and nitric acids at room temperature, glassy carbon is unaffected by such treatment, even after several months. This property makes glassy carbon a useful material for crucibles. It is also used widely as an electrode material in electrochemistry, and its biocompatibility makes it a potential component of prosthetic devices.

The structure of glassy carbon has been the subject of research since it was first produced in the early 1960s. Some of the earliest structural models assumed that both sp²- and sp³-bonded atoms were present (e.g. Ergun and Tiensuu 1959). Graphitic domains were envisaged to be interspersed with tetrahedral domains, perhaps linked by short oxygen-containing bridges. These models were based primarily on an analysis of X-ray diffraction measurements and such measurements can be open to a number of interpretations. It should be noted that neutron diffraction data have shown a complete absence of tetrahedrally bonded domains in glassy

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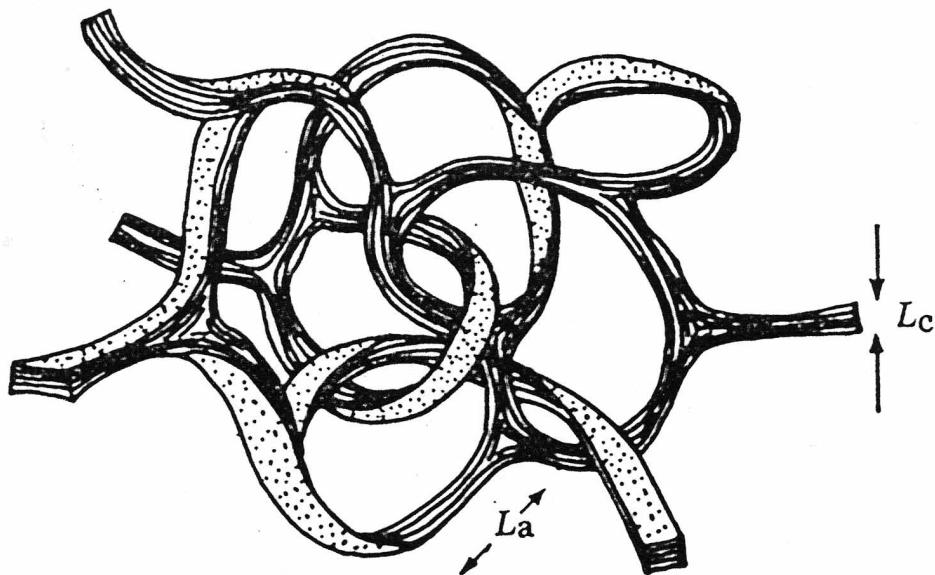


Figure 1. The Jenkins-Kawamura model of glassy carbon. L_a and L_c are the lengths of the graphitic domains perpendicular and parallel to the graphite c axis. Reproduced from Jenkins, G. M., and Kawamura, K., 1971, *Nature*, **231**, 175, with permission of Nature Publishing Group.

carbon heat treated at 2000°C (Mildner and Carpenter 1982). A different model for the structure of glassy carbon was put forward by Jenkins and colleagues (Jenkins and Kawamura 1971, 1976, Jenkins *et al.* 1972). This model, illustrated in figure 1, is based on the assumption that the molecular orientation of the polymeric precursor material is memorized to some extent after carbonization. Thus, the structure bears some resemblance to that of a polymer, in which the ‘fibrils’ are very narrow, curved and twisted ribbons of graphitic carbon. The Jenkins-Kawamura model has been quite widely accepted, but appears to be deficient in a number of aspects. For example, a structure such as that shown in figure 1, with many conjoined micropores, would be expected to be permeable to gases, whereas we know that glassy carbons are highly impermeable. The structure also has a high proportion of edge atoms, which are known to have a relatively high reactivity compared with ‘in-plane’ carbon atoms. This is inconsistent with the known low reactivity of glassy carbon, mentioned above. Recently, Russian workers have proposed a model for glassy carbon which incorporates carbyne-like chains (Pesin 2002, Pesin and Baitinger 2002). This model was based partly on a consideration of the electronic properties of glassy carbon but, as the authors themselves accept, there is no direct experimental support for their structure.

The discovery of the fullerenes (Kroto *et al.* 1985, Krätschmer *et al.* 1990) and subsequently of related structures such as carbon nanotubes (Iijima 1991) and nanoparticles (Harris 1999) has demonstrated that sp^2 -bonded carbons containing non-six-membered rings can be highly stable. This led the present author and colleagues to explore the possibility that non-graphitizing carbons may have structures related to those of the fullerenes. Detailed studies of non-graphitizing carbons prepared by

pyrolysis of sucrose and polyvinylidene chloride (Harris and Tsang 1997) were carried out using high-resolution transmission electron microscopy (HRTEM). These provided evidence for completely closed fullerene-like carbon nanoparticles, together with other features strongly suggestive of a fullerene-related structure. As a result of these observations, a model was proposed for the structure of non-graphitizing carbons which consisted of discrete fragments of curved carbon sheets, in which pentagons and heptagons were dispersed randomly throughout networks of hexagons. Subsequent work using HRTEM and other techniques provided confirmation for these ideas (Burian and Dore 2000, Harris *et al.* 2000, Burian *et al.* 2002). The aim of the present study was to examine some typical glassy carbons using HRTEM, to see whether there is evidence to support the idea that fullerene-related structures are present.

§2. EXPERIMENTAL

Four samples of commercially available glassy carbon were studied: Sigradur K and Sigradur G, supplied by Hochtemperatur-Werkstoffe GmbH, Germany, and GL-100 and GL-200, supplied by Toyo Tanso, Japan. The Sigradur carbons were prepared from phenolic resins by controlled pyrolysis in an inert atmosphere at temperatures up to 1000°C (Sigradur K) and 2800°C (Sigradur G). The Toyo Tanso carbons were also prepared from thermosetting resins, heated to 1000°C (GL-100) and 2000°C (GL-200). A further heat treatment at 3000°C was carried out on the GL-200 carbon by Iwashita *et al.* (2002) – this carbon is given the code GL-200-3000.

Samples were prepared for transmission electron microscopy by grinding gently in an agate pestle and mortar under iso-propyl alcohol, depositing the suspension onto ‘lacey’ carbon support films and allowing the solvent to evaporate. The purpose of grinding was simply to disperse the carbon in the solvent, and did not result in disruption of the carbon nanostructure or contamination. Although much of the carbon deposited in this way was too thick for detailed imaging, sufficiently thin regions around the edges of particles could readily be found. The microscopes employed were a Philips CM20 and a JEOL 2010FX, both operated at 200 kV.

§3. RESULTS AND DISCUSSION

Typical high-resolution electron micrographs of Sigradur glassy carbon K and G are shown in figures 2(a) and 2(b), respectively. In the case of the ‘low-temperature’ carbon, Sigradur K, the microstructure is disordered and isotropic, with little obvious formation of graphitic layer planes. Close examination of such images shows that the microstructure consists of tightly curled single carbon layers which enclose micropores of the order of 1 nm in diameter. In the ‘high-temperature’ carbon, Sigradur G, larger pores, around 5 nm in size, are present. These are bounded by faceted or curved graphitic walls typically containing two to four layer planes. An example of an apparently closed carbon nanostructure from the Sigradur G carbon is shown in figure 3(a). This resembles a rather imperfect multi-layered giant fullerene. There was evidence that much smaller fullerenes, similar in size to C₆₀, were also present; two such particles can be seen in figure 3(b), attached to the end of a structure which resembles a carbon nanotube.

The low-temperature Toyo Tanso carbon, GL-100, was very similar in appearance to Sigradur K, and is not shown here. An image of the high-temperature Toyo Tanso carbon (GL-200-3000) is shown in figure 4. Here the graphitic structures

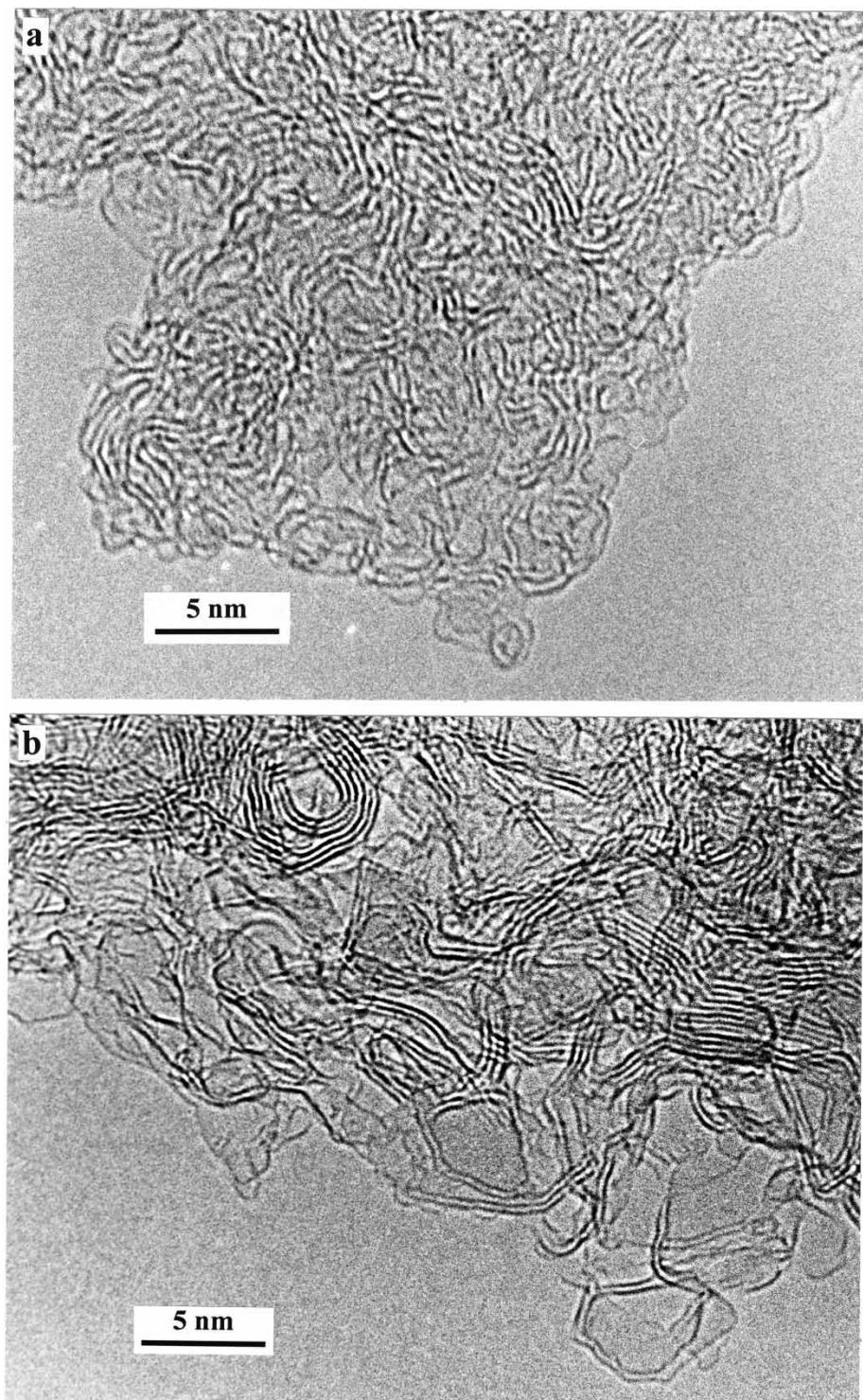


Figure 2. TEM images of (a) Sigradur K glassy carbon (prepared at 1000°C), (b) Sigradur G glassy carbon (prepared at 2800°C). The magnification is the same for both images.

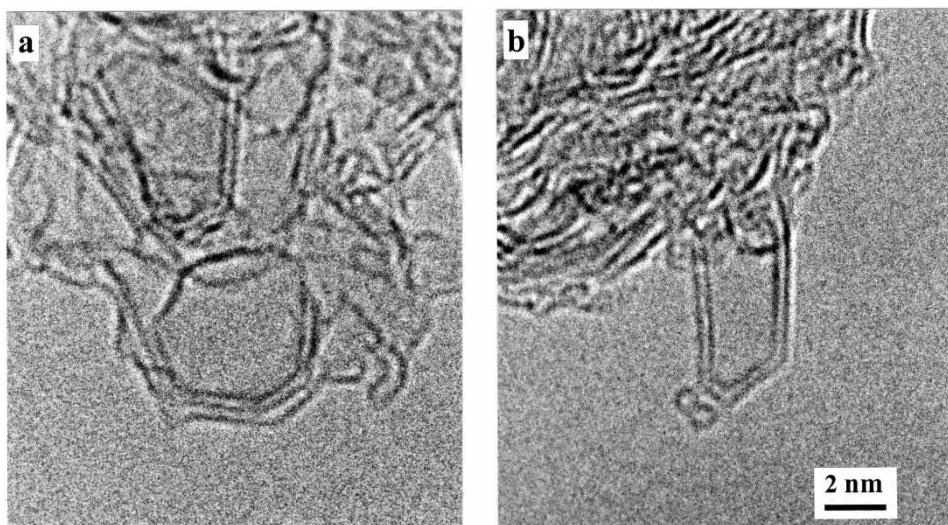


Figure 3. Nanostructures in Sigradur G carbon. (a) Imperfect nanoparticle, (b) nanotube-like structure with small fullerene particles at tip.

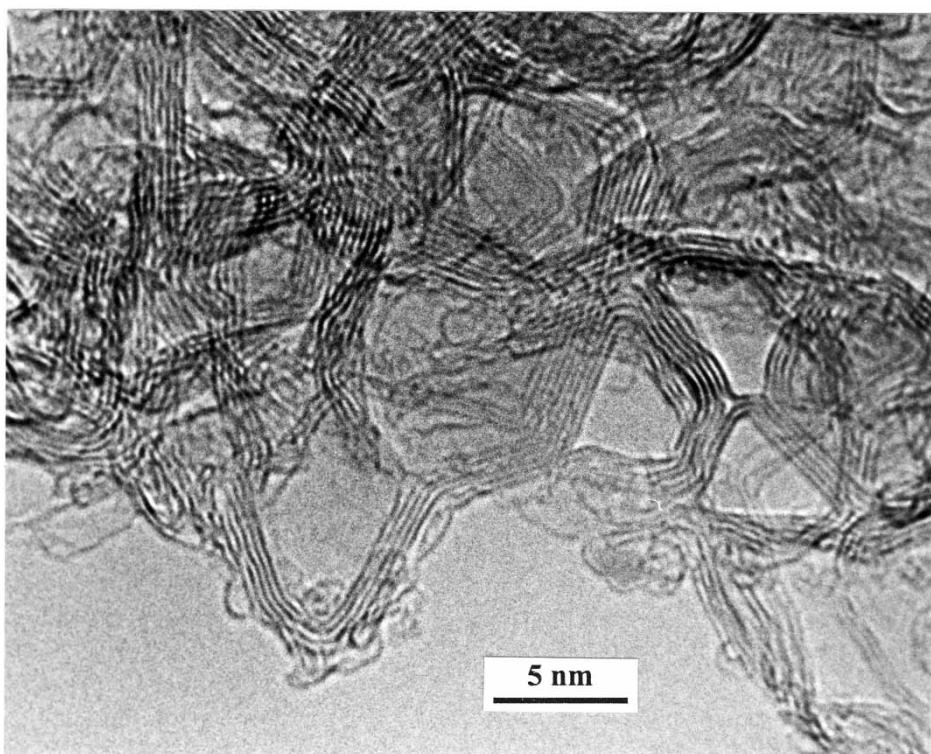


Figure 4. Image of Toyo Tanso glassy carbon GL-200 heated to 3000°C.

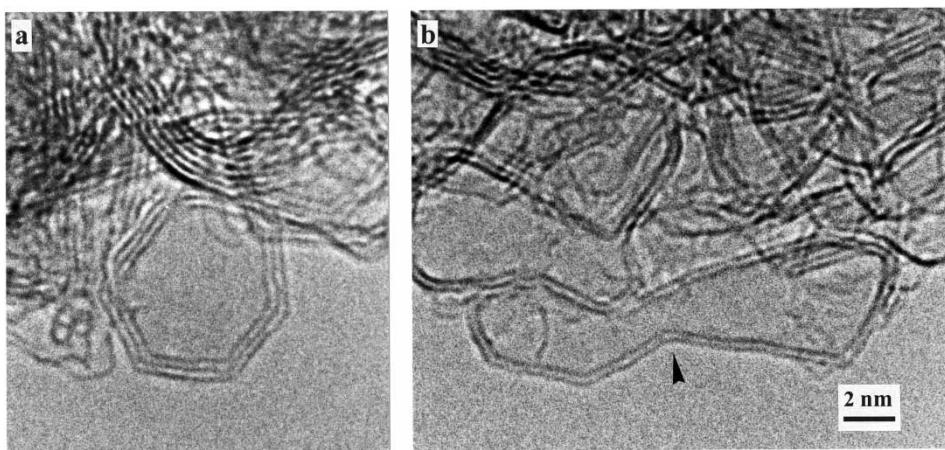


Figure 5. Nanostructures in Toyo Tanso glassy carbon. (a) Hexagonal nanoparticle, (b) closed structure with re-entrant feature indicative of heptagonal carbon ring. The magnification is the same for both images.

contain rather more layers than in the Sigradur G, reflecting the slightly higher temperature that the carbon has experienced. Completely closed particles could be found quite easily in this carbon; an example is shown in figure 5(a). These nanoparticles are rather similar to particles which can be produced by arc-evaporation in a fullerene generator (e.g. Harris 1999), although in the latter case the particles usually contain many more layers. As in the Sigradur G carbon, there was some evidence for smaller fullerenes – a possible cluster of these can be seen to the left of the hexagonal particle in figure 5(a). In addition to the closed particles, there were other features which were indicative of a fullerene-related structure. Re-entrant features were quite commonly seen, as in figure 5(b). These structures are evidence for the presence of seven-membered rings, which produce negatively curved structures, or saddle-points (Iijima *et al.* 1992).

The presence of fullerene-like structures in the high-temperature carbons suggests that glassy carbons, like other non-graphitizing carbons, may have fullerene-related microstructures. As mentioned in the Introduction, the present author and colleagues have proposed a model for the structure of non-graphitizing carbons which consists of fragments of curved carbon sheets, containing pentagons and heptagons as well as hexagons (Harris and Tsang 1997). It seems likely that the low-temperature glassy carbons studied here may have structures like that shown in figure 6(a). A distinguishing feature of glassy carbon, compared with some other non-graphitizing carbons, is low reactivity. This may result from a higher proportion of completely closed particles, or a more tightly packed microstructure, than in other carbons, making the material impermeable with lower reactivity. A model for the structure of high-temperature glassy carbon is shown in figure 6(b). This can be thought of as mainly consisting of broken or imperfect fullerene-related nanoparticles, most of which are multilayered, enclosing pores which are much larger than in the low-temperature glassy carbons. The presence of seven-membered rings produces some saddle-points in the structure. A few completely closed nanoparticles will also be present.

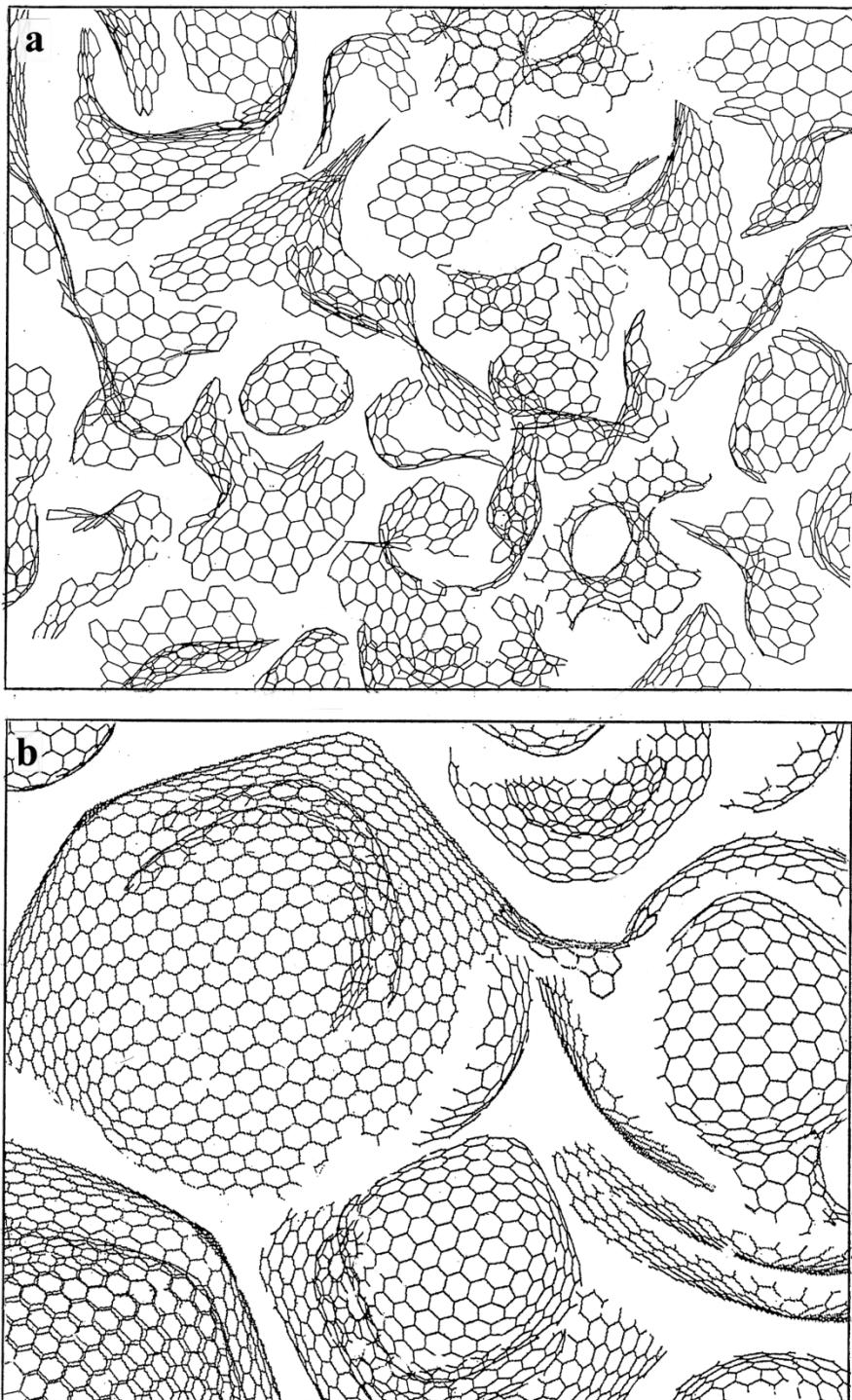


Figure 6. Models for the structure of (a) low-temperature and (b) high-temperature glassy carbon. These simulations were produced on a PC using the simple molecular modelling programme Desktop Molecular Modeller (Polyhedron Software Ltd.).

A model of heat-treated glassy carbon which also involves cage-like components was put forward by Shiraishi (1984). In this structure the particles are multilayered and have inner cavities approximately 5 nm in diameter. This model was put forward before the discovery of C₆₀, and the possibility that the cages might contain non-six-membered rings was not considered.

§4. CONCLUSIONS

The discovery of C₆₀ prompted much speculation that well-known forms of carbon may have fullerene-related structures (Harris 2003). Initially, most of this speculation centred on spheroidal structures such as soot and carbon black particles. However, there are now good reasons to believe that fullerene-related structures may be present in other well-known carbon materials such as non-graphitizing carbon. In this paper, it has been shown that glassy carbons contain many features which are indicative of a fullerene-related structure. These include faceted structures, completely closed particles and negatively curved features. As a result of these observations, new fullerene-related models have been put forward for low-temperature and high-temperature glassy carbons. These appear to have significant advantages over earlier ideas about the structure of these carbons, such as those put forward by Jenkins and Kawamura. The fullerene-related models provide a more realistic explanation for the low reactivity, hardness and impermeability of glassy carbons. It should be stressed, however, that there is no *direct* proof that glassy carbons contain pentagonal rings, and achieving such evidence will not be easy. Diffraction methods do not provide unequivocal evidence that pentagons or other non-hexagonal rings are present. In principle, modern high-resolution transmission electron microscopes should be capable of imaging individual pentagonal rings, but this would be pushing their capability to the limits. Recent work by Colliex and colleagues has suggested that electron energy loss spectroscopy might be capable of detecting individual pentagons (Stephan *et al.* 2002), but as yet there is no clear evidence for this. The apparent presence of small fullerenes in some of the carbons suggests that it may be possible to extract C₆₀ from commercial glassy carbons: this would provide strong evidence that the carbons have a fullerene-related structure. It is also worth mentioning interesting work by Gogotsi *et al.* (2000), which has shown that that Toyo Tanso glassy carbon can contain polyhedral graphite crystals, some of which resemble giant nanotubes. Such crystals were not seen in the present study, but their presence in glassy carbon is a further indication that it may have a fullerene-like structure.

Despite the progress which is being made in understanding their structure, there remain many unanswered questions about glassy carbons. In particular, it would be of great interest to know more about the mechanism whereby 'low-temperature' glassy carbon is transferred into the 'high-temperature' structure. The high-temperature carbons appear to have many fewer pentagons and other non-six-membered rings than the low-temperature carbons. Thus, during heat treatment, some pentagons must be converted into hexagons, or destroyed, while others migrate to the vertices of nanoparticle-like structures. The mechanism of pentagon migration may involve the Stone-Wales rearrangement (Stone and Wales 1986), which has been invoked to explain fullerene isomerization, but more work on the mechanisms whereby pentagons and other non-hexagonal rings can migrate is needed. It is also interesting to note that the pore sizes in the glassy carbons do not grow continuously with increasing heat treatment, but reach a constant size of approximately 5–10 nm, suggesting that fullerene-related nanostructures of this size range may have

a special stability. This is another area where more theoretical work would be of value.

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