

Homogeneous and Heterogeneous Graphitization of Carbon

It is well known that, on heating to temperatures between 1,700° and 3,000° C., some carbons show a continuous and homogeneous development of the three-dimensional structure of graphite, whereas in others the structure does not develop beyond the stage of small regions of 'turbostratic'¹ order. It has been shown² that graphitization is impeded when there is strong cross-linking between the small ordered regions (which are formed in all carbons at low temperatures), and also when there is random orientation between neighbouring ordered regions. Of these two factors, the latter is the more fundamental. At sufficiently high temperatures, cross-linking is always destroyed²; but, where random orientation exists, no homogeneous graphitization occurs.

In most non-graphitizing carbons, however, a small quantity of highly graphitic carbon is formed, as a separate phase, at some temperature above 2,000° C. This phenomenon has been interpreted in the following way³. When a carbon in which the ordered regions are strongly cross-linked in three dimensions is heated to high temperatures, great internal stresses develop; the system of cross-linking imposes a low overall thermal expansion, whereas the expansion coefficient of the ordered regions must be at least as great as that of graphite. This results in local breakdown of the cross-linking, followed by a corresponding local crystallization of the carbon under pressure, the process continuing until the internal stresses have been relieved to such an extent that no further breakdown of the cross-linking occurs.

Thus, we see that, although cross-linking prevents the homogeneous development of a graphitic structure, it promotes the heterogeneous formation of a small quantity of highly graphitic carbon in non-graphitizing carbons.

The above observations provide a possible explanation of some results obtained in an investigation of the influence of the oxidation of a coal on the graphitization of a coke prepared from it.

A coking coal which normally yielded graphitizing carbons was oxidized in air at 110° for periods up to twenty days. Samples withdrawn after different periods of oxidation were then heated at 2,700° C. It was found that short periods of oxidation of the coal (up to about five days) decreased the graphitization of the carbon. After longer periods, however, the graphitization again increased, but it now occurred heterogeneously instead of homogeneously; the X-ray diffraction patterns of the carbons showed clearly the presence of a mixture of highly graphitized and non-graphitized material (cf. ref. 2) rather than a single, partially graphitized phase³.

These results suggest that mild oxidation of a coal leads to cross-linking which inhibits crystallite growth in the carbon, whereas in carbon formed from strongly oxidized coals the system of cross-linking is so strong that heterogeneous graphitization is promoted.

This interpretation was confirmed by a similar series of measurements made on a non-graphitizing coal oxidized in air at 110° C. for periods up to sixty days, and afterwards heated to 2,700° C. Both the raw coal and the coal oxidized for four days yielded carbons which showed neither homogeneous nor heterogeneous graphitization. A trace of heterogeneously formed graphitic carbon was first observed

in the sample oxidized for fifteen days. Longer periods of oxidation resulted in the heterogeneous formation of larger quantities of graphitic carbon, the proportion reaching 9 per cent after sixty days of oxidation. Thus in this case, again, the strengthening of cross-linking brought about by oxidation increased the heterogeneous formation of graphitic carbon.

It therefore appears that graphitization can occur by two quite distinct processes. Homogeneous graphitization occurs in carbons in which neighbouring ordered regions lie in near-parallel orientation, and in which cross-linking is weak³. Heterogeneous graphitization results when cross-linking is so strong that, when it starts to break down at high temperatures, localized forced crystallization under pressure occurs.

Since heterogeneous graphitization involves the breakdown of cross-linking, it sets in at a higher temperature than homogeneous graphitization. The graphitic product, however, is more highly graphitized than a product of homogeneous graphitization at the same temperature, since it is crystallized under pressure.

The experiments described above were carried out during 1950 at the Laboratoire Central des Services Chimiques de l'État, 12 quai Henri IV, Paris. I am indebted to M. J. Méring for many helpful discussions.

ROSALIND E. FRANKLIN

Birkbeck College Crystallography Laboratory,
21 Torrington Square,
London, W.C.1.
Sept. 7.

¹ Biscoe, J., and Warren, B. E., *J. App. Phys.*, **13**, 364 (1942).

² Franklin, R. E., *Proc. Roy. Soc., A*, **209**, 196 (1951).

³ Franklin, R. E., *Acta Cryst.*, **4**, 253 (1951).

Diffusion of Interlayer Water in Vermiculite

A CONVENIENT optical method for studying the diffusion of water molecules in vermiculite is outlined below. The effect has similarities to that employed by Tiselius¹ in his studies of diffusion in the zeolites; but, in this instance, it can be observed in reflected or transmitted light and is not a birefringence effect. Although magnesium vermiculite is referred to particularly, vermiculites saturated with cations other than magnesium behave in a similar (although not identical) manner.

When a flake of magnesium vermiculite, which has been partially dehydrated to the phase containing single sheets of interlayer water molecules ($d_{001} = 11.59$ Å.), is allowed to become rehydrated, a dark line is observed to enter the flake at the edges and gradually converge on the centre. Inspection under the microscope reveals that the first moving boundary is followed by a second which is much fainter and travels at a slower rate (Fig. 1). These boundaries represent wave-fronts of water molecules diffusing into the crystal. The first and stronger of the two is caused by a phase change corresponding to an expansion of the lattice in the *c*-direction from 11.59 Å. to 13.82 Å., and the second by a smaller lattice expansion from 13.82 Å. to 14.36 Å.² The reverse process, namely, dehydration, is rather more difficult to observe.