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Bragg, R.H.

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Presented at the 3rd International Conference on
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R.H. Bragg

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GLASS-LIKE CARBON:
A C₃H POLYMER INTERCALATION COMPOUND^Δ

Robert H. Bragg

Materials and Molecular Research Division
Lawrence Berkeley Laboratory and
Department of Materials Science and Mineral Engineering
University of California
Berkeley, California 94720
U.S.A.

ABSTRACT

The structure and annealing behavior of glass-like carbon show that it is a polymer carbon but similar to other carbons that have been extensively studied. X-ray and neutron diffraction indicate a crystallite size of 2.0 to 5.0 nm, but lattice fringe images show continuous interwound laths made up of 5-10 layers of graphite planes. During heating above about 2000°C, the interlayer spacing decreases, hydrogen is removed, and the sign of the Hall coefficient changes. It is proposed that these phenomena indicate de-intercalation of hydrogen from an intercalation compound of stage 1 composition C₃H.

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I. INTRODUCTION

Carbons are defined as solids prepared by the thermal decomposition of a hydrocarbon by heating, usually in inert atmosphere, in the range 500-1000°C, or deposition from the vapor phase of hydrocarbon, typically methane, on a heated substrate at temperatures around 2000°C.¹ The initial chemical composition is about 95 to 97 percent carbon and the balance is hydrogen. Glassy carbon GC is made by carbonizing a thermosetting resin. At this stage there is no evidence of crystallinity revealed by light or electron microscopy, i.e., there are no grain boundaries in the sense of polycrystalline materials. The diffraction pattern consists of diffuse but symmetrical 002 reflections and asymmetrical hK bands.² Heating in the range 1000-1800°C causes a narrowing of the diffraction line profiles, but the interlayer spacing $\bar{d}_{002}$ remains at 0.344 nm even after 156 hours.³ During heating above 2000°C, the interlayer spacing decreases and lattice images of 002 graphite planes can be formed (Fig. 1). They show a polymeric structure of interwound laths composed of stacks, 10 to 20 layers thick of graphite planes. This paper advances the hypothesis that GC, in common with other carbons, is an intercalation compound C_xH , and the changes in structure and physical properties induced by heating at high temperatures are associated with de-intercalation.

II. CRITERIA FOR IDENTIFYING A GRAPHITE INTERCALATION COMPOUND

The most important properties of an intercalation compound are the retention of the structure of individual layers; a change in layer spacing, usually an increase; and a change in electrical properties. A binary system of graphite and say an alkali or a halide will have a phase diagram consisting of single or two phase regions where the phases consist of stage compounds, e.g., C_8K for stage 1, or mixtures of stages. A stage has a well defined interlayer spacing which is unchanged over a range of composition. At equilibrium, a mixture of stages will

have a diffraction pattern which is a superposition of the individual patterns. If a stage 1 compound say, is de-intercalated under nonequilibrium conditions, the diffraction pattern often indicates the coexistence of several stages. Intercalation usually has a dramatic effect on electrical properties. The electrical conductivity parallel to the layer planes increases many-fold, and the majority carrier may be changes, i.e., the sign of the Hall coefficient, as well as its magnitude is changed, indicating a transfer of charge either from the donor to the graphite layers, or a removal of charge from the layers to the acceptor.

III. EVIDENCE FOR THE INTERCALATION OF HYDROGEN IN CARBONS

Thus far there are no known instances of the direct intercalation of hydrogen into graphite, but the indirect evidence is considerable. Radial distribution analyses show that in all carbons, the integrity of the layers, i.e., the carbon-carbon distances within layers is not changed despite the degree of stacking disorder.

If hydrogen were intercalated into graphite, the interlayer spacing for stage 1 could be estimated from the expansions caused by alkali or halide intercalants. Figure 2 shows a graph of stage 1 interlayer spacings plotted versus ionic radii for both. If it is allowed that hydrogen can be present as H^+ or H^- then the observed 0.344 nm spacing (proposed herein to be characteristic of stage 1) requires an ionic radius of about 0.05 to 0.06 nm. Alternatively, if the 0.344 nm is taken as the stage 1 spacing, a radius of 0.055 nm is calculated for the intercalant. If there is no stacking disorder then de-intercalation should result in higher order stages and larger d-spacing in the diffraction patterns. Careful experiments done by Fischbach⁴ and by many workers in the Bordeaux group show⁵ that during isothermal annealing above about 2000°C, the mean interlayer spacing

decreases below the 0.344 nm, but plateaus or steps are observed. It is suggested that during de-intercalation equilibrium conditions are not obtained, and because of disorder in the sequence of layer spacings, an average representing the relative frequencies of stage 1 and pristine graphite is observed.

Oberlin and Mering showed that under certain conditions direct chemical treatment leads to structures corresponding to 4 different kinds of defects and d-spacing.^{6,7} The defects were thought to be interstitial carbon, but the data are more consistent with hydrogen. Neutron diffraction experiments show that a strong incoherent scattering which could only come from hydrogen is present in the patterns of samples heated at 1000°C, but is reduced by heating at 2500°C and direct measurements of total neutron scattering cross sections confirms the reduction in hydrogen content.³ The kinetics of weight loss has also been studied, and it is consistent with the diffusion of hydrogen in the layer plane direction.^{8,9}

Studies of the electrical properties of carbons show that they satisfy the electronic criterion for an intercalation compound. Prior to the work on GC, for example, Flandrois and Tinga found that during isothermal annealing of a pitch coke in the range 1420 to 2850°C, the Hall coefficient, originally negative, becomes positive and ultimately negative again.¹⁰ In this work, steps were also observed in $\bar{d}_{002}$. In the experiments on GC, a change in the sign and magnitude of the Hall coefficient is also observed^{11,12}, Fig. 3, but thus far there is no clear evidence for steps or plateaus in $\bar{d}_{002}$. However, the evolution of structural change in GC is so slow and the steric hindrances are so great (Fig. 1), that observation of plateaus are not likely with reasonable limits on the time of heat treatments.

IV. THE PROBABLE CHEMICAL COMPOSITION OF STAGE 1 C_xH

The chemical composition of the proposed stage 1 compound can be estimated from the work of Carmona and Delhaes.¹³ They found that the density of anthracene char heated to 1500°C, which would correspond to stoichiometric stage 1 C_xH was 5 percent less than that of ideal graphite (2.26 gcm^{-3}). Full densification, during which d_{002} undergoes a 2.5 percent decrease implies a 2.5 percent loss of weight. Thus the molar ratios of carbon to hydrogen at stage 1 are about 97.5/2.5 to 2.5/1. Thus, allowing for experimental errors in the density measurement, $\pm 0.005 \text{ gcm}^{-3}$; it appears that the composition of stage 1 is about C_3H .

V. SUMMARY AND CONCLUSIONS

From the foregoing, it appears that the annealing behavior of carbons is consistent with the de-intercalation of an intercalation compound of stage 1 composition C_3H with kinetics controlled by the out-diffusion of hydrogen. This model, through backing in specific structural detail explains phenomena which have long puzzled carbon specialists who use the collective term "graphitization" to identify them.⁴ Plateaus or steps in d_{002} and other physical properties are predicted by the model. It explains why certain gases or solids, e.g., oxygen or Cr_2O_3 catalyze the process. It even predicts an inverse relationship between the width of graphitic layers and the mean interlayer spacing. Definitive experiments are required to test the hypothesis. The most obvious, direct synthesis and characterization are in progress.

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(a)

(b)

(c)

(7)

XBB 810-12199

Figure 1

Lattice images of 002 planes in glassy carbon.
Heat treatment at 2700°C.
Underfocussed; focussed; overfocussed.
The layer spacing is 0.34 nm.

XBL 8210-6712A

Figure 2
 Layer spacing of Stage 1
 compounds versus ionic radius.

Figure 3

Hall coefficient versus heat treatment
temperaute in glassy carbon.

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