Nanostructural development of non-graphitising carbons probed using TEM/EELS: the importance of fullerenes?

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Abstract. This work presents a comprehensive study of a set of non-graphitising carbons as a function of heat treatment temperature (HTT) up to 3000 °C using a combination of density measurements, X-ray and electron diffraction, high resolution TEM and low loss and core loss EELS. Results are compared to those obtained from graphitising carbons. Of interest is the variation in plasmon energy with HTT and its relationship to density as well as the ratio of sp² to sp³ bonded carbon species derived from the C K-edge using a revised analytical procedure. Results are reviewed in light of the fairly recent suggestion that the intrinsic structure of non-graphitising carbons is based on the inclusion of fullerene-like units. We speculate as to whether this might have a broader significance for carbonaceous materials in general.

1. Introduction

Carbon materials are highly versatile owing to the strong dependence of their physical properties on the ratio of sp² (graphitic) to sp³ (adamantine) bonds. Graphitic carbons have a variety of forms with various degrees of ordering ranging from microcrystalline graphite to glassy carbons. Amorphous carbons can have any mixture of sp³, sp² and, in some cases, sp¹ bonded carbon sites with the additional possible presence of hydrogen, nitrogen or boron. The structure of amorphous or poorly crystalline carbon materials are difficult to study using conventional characterisation tools, although neutron scattering, nuclear magnetic resonance, (uv) Raman spectroscopy and EELS all show promise.

Non-graphitising (NG) carbon materials are hard, low density materials which fail to pass through a liquid stage upon heat treatment and do not ultimately form crystalline graphite at temperatures in the region of 3000 °C. Instead they largely retain a hard, entangled ribbon-like structure containing micropores < 2 nm in diameter. This microstructure is fixed by the cross-linking of the polymer chains within the precursor and traditionally this high surface area microporous structure has been viewed as consisting of twisted networks of carbon layer planes cross-linked by bridging groups. However, more recently a fullerene-like structure has also been proposed from high resolution electron microscopy data [1].

As a typical non-graphitiisable carbon, phenolic resin is commonly used in carbon/carbon composite materials or as a refractory binder owing to its homogeneous, isotropic properties. During heating, phenolic resin is gradually transformed from a polymer to a hard, glass-like isotropic carbon containing some microporosity. The purpose of this study is to shed light on the evolution of the nanostructure and chemical composition of a phenolic resin, during the heat treatment process, ultimately in order to try and explain the observed macroscopic properties.
2. Experimental
A resol-type phenolic resin (SC 1008 - Borden Chemicals UK Ltd.) was subjected to different heat treatment temperatures (HTT) between 600 °C and 2000 °C for 2 hours under a N₂ atmosphere; the heating rate was either 1 °C/min for temperatures < 1300 °C or 500 °C/h for temperatures ≥ 1600 °C. Two additional samples were also high temperature heat treated using different heating profiles up to a maximum temperature of 2500 °C and 3000 °C respectively. The samples heated to temperatures ≤ 1000 °C were initially cured at 260 °C in order to remove volatile species, while those heated to temperatures ≥ 1300 °C were correspondingly cured at 1000 °C. After each heat treatment, the percentage mass loss and density (both Archimedes and Helium) of samples were determined, as well as the sample surface area and pore size distribution using nitrogen gas adsorption.

TEM analysis was conducted on an FEI CM200 FEG TEM running at 197 kV equipped with an Oxford Instruments EDX spectrometer and a Gatan Imaging Filter. Samples were prepared by dispersing in methanol, with a drop placed on a holey carbon coated copper grid. Powder XRD was also performed using a Philips APD 1700 diffractometer and Cu Kα radiation.

3. Results and Discussion
The volume plasmon in the EELS spectrum arises from a collective oscillation of the entire valence electron population and, in the free electron model the plasmon peak energy is proportional to the square root of the valence electron density. Figure 1a shows the variation of the valence plasmon peak energy, Eₚ, (extracted from the first derivative of the spectra) with different HTT of the phenolic resin samples, the error bars represent the standard deviation of 10 measurements from each sample. It is apparent that the plasmon peak position remains unchanged or even slightly decreases with increasing HTT, this behaviour tracks the sample density which remains relatively constant (figure 1b) or actually falls during heat treatment; as a result of the formation of closed fullerene-like loop structures. By 1300 °C, clear (002) type lattice fringes are apparent with layer packets of thickness 3-4 layers and 3-4 nm in lateral dimension being visible. In addition pores a few nanometres in diameter are evident. These layer packets order and become straighter at 1600 °C (figure 2c), whilst at 2000 °C and above (Figure 2d-e) circular and elongated closed loop structures some 5-6 nm in diameter become apparent with clearly visible (002) fringes and layer packets > 4-5 layers begin to form. The images at temperatures > 2000 °C are somewhat reminiscent of the structures seen by Harris and Tsang [1] in chars derived from a polyvinylidene chloride (PVDC)- polyvinylchloride (PVC) copolymer and also sucrose after pyrolysis at 2100 - 2600 °C.

The TEM images are in reasonable quantitative agreement with the XRD data at these temperatures; with increasing HTT, the (002) layer spacings are observed to progressively decrease and the layer stack coherence length Lₙ progressively increase up to ca. 8 nm. Furthermore, N₂ gas adsorption shows a maximum in pore volume for the 800 °C sample corresponding to a minimum in the pore width. Above this HTT, the pore width was observed to increase up to a maximum value at 1300 °C and then decrease again, with the corresponding pore volume going through a minimum at this temperature presumably arising as a result of increasing closed porosity from the formation of fullerene-like units.
Figure 1. (a) Plasmon peak position (b) density of phenolic resin as a function of HTT.

The EELS carbon K-edges from the phenolic resin samples heat treated at different temperatures, show two main features: a $\pi^*$ peak at 285 eV followed by a $\sigma^*$ peak at ca. 290 eV and above. With increasing HTT, the relative $\pi^*$ peak intensity is observed to increase and the $\sigma^*$ structure becomes more well defined. Quantitative analysis of carbon bonding using EELS may be achieved using procedures outlined in reference [3]. Briefly the $1s$ to $\pi^*$ peak intensity at the C K-edge (background stripped and deconvoluted to remove plural scattering), $I_{\pi^*}$, is measured using a Gaussian fitting procedure and ratioed to the total C K-edge intensity in a window of up to 20 eV extending from the edge onset. This intensity ratio is normalized to a reference spectrum containing 100% sp$^2$ bonding (highly oriented pyrolytic graphite). The normalized intensity ratio can then be used to obtain the sp$^2$ fraction, provided the different carbon bonding states are known, e.g. just sp$^2$ and sp$^3$. An example fit is shown in figure 3a and the variation in sp$^2$ content during the heat treatment of the non-graphitising carbon derived using this procedure is shown in figure 3b. These results suggest that, although the overall density is reasonably constant with increasing HTT presumably due to the presence of crosslinks, the sp$^2$ content does still increase in a similar fashion to that seen in graphitising carbons [2], albeit with the development of many very small graphitic pockets rather than an increasingly larger densified graphitic structure, as is the case with a graphitising carbon [2]. In addition, there is evidence for a reduction in sp$^2$ carbon content at intermediate temperatures > 1000 °C, which could be due to puffing and disordering of layers as a result of the loss of volatiles, mass loss and a corresponding density decrease from the emergent fullerene-like structure in the microporous material. Similar layer puffing was suggested to occur in graphitising carbons due to the loss of heteroatoms at somewhat higher temperatures [2].

The fit to the C K-edge in figure 3a has employed unconstrained Gaussian fits to the following features: C=C $\pi^*$ (at ca. 285 eV), C-C $\sigma^*$ (ca. 292 eV) and C=C $\sigma^*$ (ca. 300 eV) (assignments nominally based on gas phase spectra); note that the residuals of the fit clearly show the existence of a peak at ca. 287 eV which persists even at high HTT [3]. There are a number of possible origins for this residual peak such as C-H $\sigma^*$ states or even aldehyde-type bonds. It is unlikely hydrogen persists at high temperatures, however one distinct possibility based on the high resolution TEM images is the presence of fullerenes which, on the basis of high resolution X-ray absorption spectra, would be expected to give rise to a double peaked $\pi^*$ peak with additional intensity at 287 eV [4].

In a broader context, we speculate as to whether such fullerene-like features are also present in other poorly crystalline carbon systems such as amorphous diamond-like carbon (DLC) films, glassy carbons, carbon nanostructures and even graphitizing carbons which may complicate a simplistic analysis of carbon bonding and possibly explain any discrepancies (some observed by the authors) between EELS analysis and other techniques for determining sp$^2$/sp$^3$ ratios such as uv Raman.
4. Conclusions
There appears to be evidence from HRTEM and also analysis of the EELS carbon K-edge for the presence of fullerene-like structures in non-graphitising carbons heat treated above 800-1000 °C. Fullerene-like units are expected to result in additional intensity on the high energy side of the C=C π* peak at the C K-edge and may complicate a simplistic analysis of the sp2-content in carbon materials.

References
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