

INVESTIGATING THE GRAPHITIZATION OF CARBON USING ANALYTICAL FEGTEM

H.R. Daniels, A.P. Brown, B. Rand and R. Brydson
Institute for Materials Research, University of Leeds, Leeds, LS2 9JT, UK.

Abstract. A combination of high resolution electron microscopy, electron diffraction, energy filtered imaging and electron energy loss spectroscopy on a field emission TEM has been used to study the microstructural development in graphitising carbons as a function of heat treatment.

1. Introduction

The graphitization of carbon is an important, yet sometimes difficult, microstructural process occurring during the production and processing of a large range of materials including carbon fibres and tapes, carbon nanotubes, carbon composites, carbon coatings and dispersed precipitates in cast irons and mild steels. Graphitization of carbon leads to large changes in mechanical, thermal and electronic properties and there is a need to develop accurate spatially resolved imaging and spectroscopic methods for the determination of the degree of graphitic character as a function of heat treatment, both to study the nature of the graphitization process itself as well as to extract information on the resultant physical properties of the material's microstructure.

2. Method

Samples of a petroleum-based pitch (Aerocarb 80) were heat treated in an inert atmosphere at a series of temperatures between 200°C and 2730°C. Powders were initially ground and examined by X-ray diffraction (XRD) and He density measurements. Powders were then dispersed onto holey carbon support films and thin areas examined in a FEI CM200 FEGTEM fitted with a GIF 200 using HRTEM, selected area electron diffraction (SAED), EELS and EFTEM.

3. Results and Discussion

XRD, SAED and HRTEM imaging do provide a (well documented) means of tracking the graphitisation process. XRD can provide averaged values for the (002) interlayer spacing and also, from the widths of diffraction peaks, the crystallite dimensions (L_a and L_c). SAED produces spatially resolved data on the (002) spacing, its variation and also the angular deviation of basal planes from a perfectly planar configuration. HRTEM can image (002) basal planes directly and also provide a direct indication of crystallite size [1]. Generally the interlayer spacing decreases monotonically with increasing heat treatment temperature, whilst the crystallite size correspondingly increases. Some important findings from these comparative studies include: the presence of significant structural heterogeneity within samples heat treated at a particular temperature (that appeared to be correlated with the presence of S and Si heteroatoms which are known to promote cross-linking and inhibit graphitization) and, secondly, slight variations in the

monotonic trend at intermediate temperatures (ca. 1500°C) which may be linked to the loss of heteroatoms and subsequent “puffing” of graphene layers.

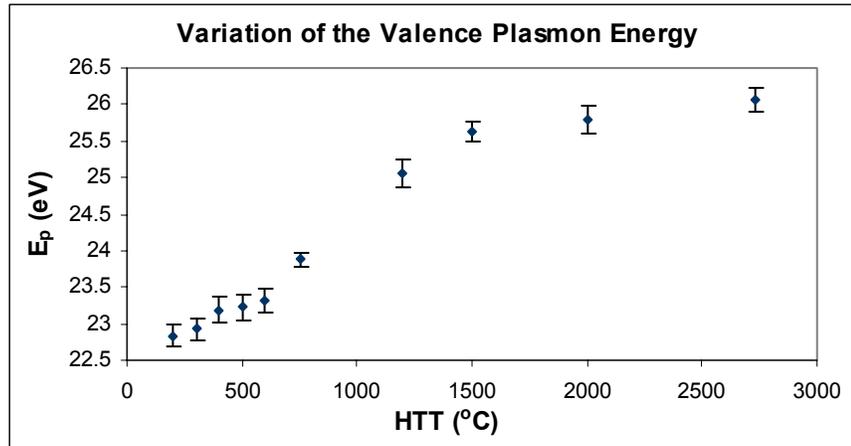


Figure 1. Variation of the volume plasmon energy with heat treatment temperature.

EELS measurements can also provide important additional information on the graphitisation process. Figure 1 shows the variation in the volume plasmon energy of the graphitisation series as a function of heat treatment temperature. Each data point is the average of at least ten measurements. In a free electron model, the volume plasmon energy scales as the square root of the valence electron density and accordingly this data shows an excellent linear correlation with the square root of the He density measurements. The plasmon energy thus provides a sensitive measure of the degree of graphitic character and it is possible to use an EFTEM technique to image variations in graphitic character within complex specimens such as carbon-carbon composites and graphitic nodules in medium carbon cutting steels. Here EFTEM images are acquired using two 3 eV windows centred at 22 eV and 27 eV in the plasmon region, the ratio of these two images providing high resolution (1.6 nm) graphitisation maps free from diffraction (i.e. orientation) contrast and thickness effects [2].

Another feature in the EELS low loss spectrum is the $\pi \rightarrow \pi^*$ transition peak at ca. 6.5 eV which represents a single electron transition that exhibits significant collective (plasmon-like) character. As the degree of graphitic character increases, the proportion of planar sp^2 -bonded carbon should increase. The $\pi \rightarrow \pi^*$ peak intensity should therefore provide a measure of % sp^2 -bonded carbon when normalized to the data for 2730°C (i.e. assuming 100% sp^2 -bonded carbon at this temperature). Figure 2 shows the variation in relative $\pi \rightarrow \pi^*$ peak intensity of the graphitisation series as a function of heat treatment temperature. Again these data are averages of multiple measurements and care was taken to ensure that, under the experimental conditions employed (near parallel illumination and a collection angle, $\pi = 1.7$ mrad), this peak intensity was independent of the crystallographic orientation of the sample area [1, 3]. The data show a gradual increase in % sp^2 carbon content with temperature and an apparent dip at

1500°C, corresponding to the buckling or ‘puffing’ of the basal planes due to loss of volatiles.

The carbon K-edge in the EELS core loss region can also provide important information on the local carbon environment during the graphitisation process. Figure 3 shows the evolution of the carbon K-ELNES for the graphitisation series as a function of heat treatment temperature.

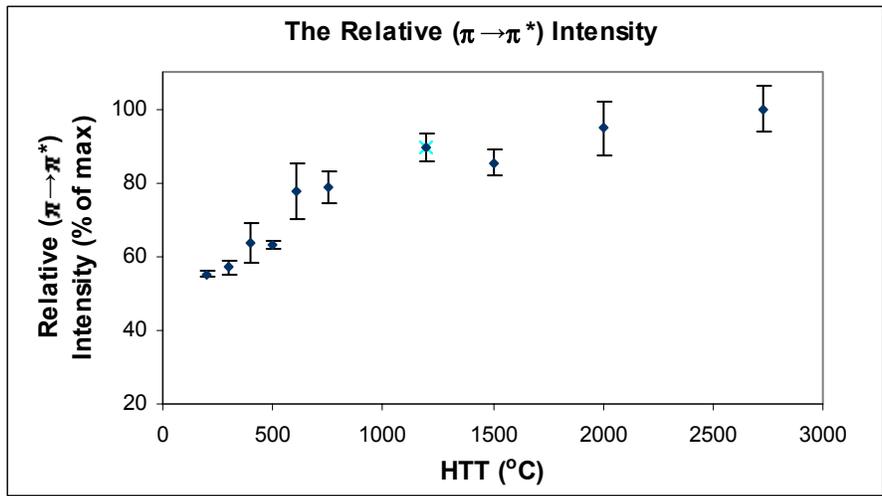


Figure 2. Variation of the relative ($\pi \rightarrow \pi^*$) peak intensity with heat treatment temperature.

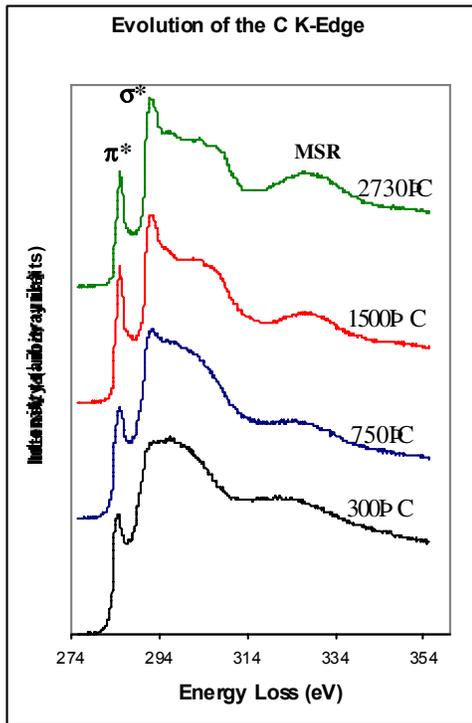


Figure 3. Evolution of C K-ELNES with heat treatment.

These spectra were measured using parallel illumination and $\pi = 1.7$ mrad, where spectra are independent of crystallite orientation [4]. The C K-ELNES exhibits a number of important features: firstly the $1s \rightarrow \pi^*$ peak at 285 eV, the $1s \rightarrow \pi^*$ region commencing at ca. 292 eV and a broad multiple scattering resonance (MSR) centred at ca. 330 eV. The exact energy position of the MSR above the edge onset is known to be proportional to the inverse square of the next nearest neighbour bond length around the carbon atom. Thus it is possible to derive the C-C bond length in the graphene sheets. Figure 4 shows the calculated variation in bond length as a function of heat treatment temperature and this correlates well with XRD and SAED data.

Figure 3 shows an increase in π^* peak intensity as graphitisation proceeds owing to the increasing proportion of sp^2 -bonded carbon, as well as a significant sharpening of the π^* structure due to increasing long range order. The relative intensity of the $1s \rightarrow \pi^*$ peak, normalized to the intensity within a 20 eV window covering both the π^* and π^* features, can be used to extract the % sp^2 -bonded carbon in a similar fashion to the low loss data in figure 2. Figure 5 shows the results of this analysis of the C K-ELNES. The trend in figure 5 is very different to that in figure 2, notably the higher values of sp^2 content derived from the core loss data. One possible reason for this is due to the significant hydrogen content present in the pitches which will result in significant C-H bonds giving rise to a $1s \rightarrow \pi^*$ (C-H) feature between 287-289 eV. Deconvoluting the effect of this additional intensity contributing to the $1s \rightarrow \pi^*$ peak we obtain the lower curve in figure 5 which is in considerably better agreement with the sp^2 contents shown in figure 2.

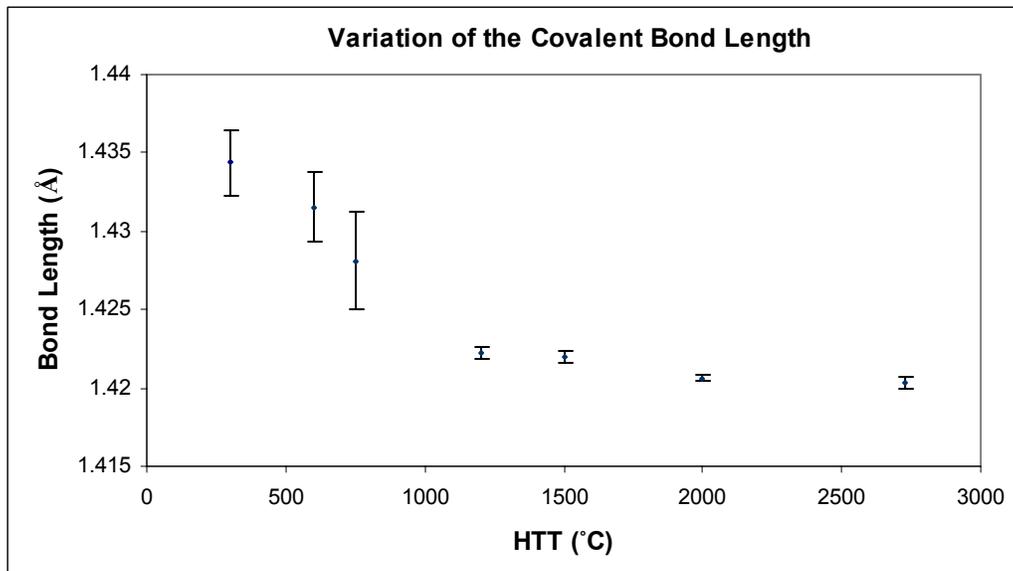


Figure 4. Variation of the C-C covalent bond length (Angstrom) as a function of heat treatment temperature.

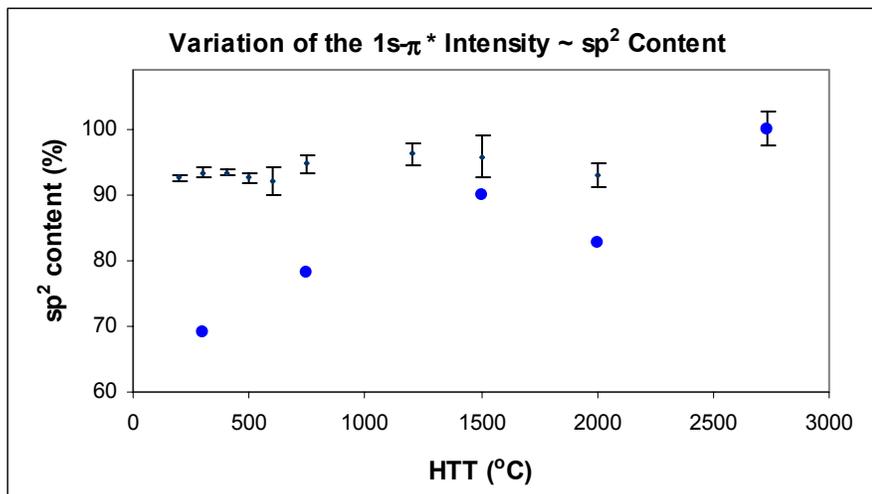


Figure 5. Variation of sp^2 C content derived from the $1s \rightarrow \pi^*$ peak intensity as a function of heat treatment (upper curve with error bars); lower curve (dots) includes a correction for C-H bonding.

4. Conclusion

EELS analysis of a series of graphitising carbons heat treated at different temperatures can provide quantitative information on the graphitisation process complementary to that derived from XRD, He density measurements, SAED and HRTEM.

5. References

- [1] Daniels H R, PhD Thesis, IMR, University of Leeds, 2003.
- [2] Daniels H R et al., Ultramicroscopy 96, 547-558, 2003.
- [3] Daniels H R et al., submitted to Carbon
- [4] Daniels H R et al., Ultramicroscopy 96, 523-534, 2003.