Surface Graphitization of Glass-Like Carbons:
Microprobe Raman Observations

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Introduction

It is well known that hard, glass-like carbons (GLCs) are paragons of non-graphitizability, due to the morphological constraints inherent in the very fine-scaled isotropic, microporous structure. Monolithic samples retain small apparent crystallite size with no evidence of regular layer stacking order, and properties characteristic of very disordered structures even after processing to heat treatment temperatures HTT ≥ 3000 C [1-7]. On the other hand, it is also well established [2,8,9] that when finely powdered hard carbons such as GLC are heated above some critical temperature (≳2000 C), a small portion of the material transforms abruptly to graphite plus a graphitizable turbostratic form (multiphase graphitization). This transformation initiates on the particle surfaces [9], enabled by the relaxation of microstructural constraints.

It might be expected that graphitization would also occur on the free surfaces of monolithic GLC. Some support for this is provided by reports of optically anisotropic pore walls, weak graphite spikes on the broad (002) XRD peak and positive magnetoresistance after high HTT in macroporous, low-density GLCs [10,11]. Direct evidence for significant evolution of the surface structure of normal-density GLCs was obtained using ordinary Raman spectroscopy [6]. This paper presents the results of a more extensive characterization of GLC surface structures by microprobe laser Raman scattering.

Characterization of Carbons by Raman Spectroscopy

The spectra of carbon materials result from the inelastic scattering of optical photons by in-layer phonons, within a depth of ≲ 100 nm. The spectrum of crystalline graphite consists of a first-order line G at ~1580 cm^{-1}, and an asymmetric doublet G'$_{(1,2)}$ at ~ 2700 and ~2735 cm^{-1} (plus weak features at ~2450 and ~3250 cm^{-1}) in the second-order range. In disordered carbons, due to the relaxation of symmetry selection rules, additional bands occur at ~1350 (D),~1620 (D') and sometimes ~2950 cm^{-1}; G is shifted to slightly higher frequency; and all lines are broadened, the G' doublet fusing into a single symmetrical band at ≈2710 cm^{-1} [5,6,12]. Spectral parameters that are useful for assessing carbon structural development include the positions ν, widths W, integrated intensities I and shapes of these bands. The intensity ratio I_D/I_G is a measure of layer size and perfection, but is insensitive to stacking order. Lespade et al. [12] found that ν_G and W_G are also good indicators of 2-dimen-

sional structural development, whereas evolution of the G' doublet indicates layer stacking order. Thus, Raman spectroscopy is a very useful tool for characterizing the near-surface structures of carbons. Both as-heat-treated surfaces and brittle fracture surfaces are suitable for studying the undisturbed structure [5,6].

Experimental Procedure

The GLCs studied were obtained from Beckwith Carbon (B) and Sigri Electrographit (S) as 3 mm thick plates. The bulk graphitization behavior of these carbons was studied earlier in terms of density [4], magnetic susceptibility [7], and Raman spectra [5,6]. In the present work, small samples were heated in graphite crucibles in a graphite resistance furnace in He for 30 min at 2200 - 3000 C. These samples were then crushed and spectra were obtained from both the heat-treated exterior (E) surfaces and the interior-material fracture (F) surfaces using a Jobin-Yvon MOLE Raman microprobe with 514.5 nm laser excitation and a 100x objective lens (<3 μm spot size). The short working distance of this lens restricted the selection of measurement positions on the irregular F surfaces; but lower magnifications resulted in poor-quality spectra. The spectra were analyzed in terms of the ν, W, I and qualitative shapes of the G (1580), D (1350) and G' (2700 cm^{-1}) bands. The G data included contributions from the unresolved D' band. I values were determined by weighing cut-out tracings.

Results and Discussion

Spectra obtained from the heat-treated E surfaces showed progressive graphitization with increasing HTT, and were insensitive to location on the sample. The F surfaces, intended to present interior material, generally had much more disordered structures but there was considerable variation at high HTT. Evolution of the structures toward that of graphite was indicated by: a) decreasing I of the D' shoulder of G, and of D; b) narrowing of G and D, and a gradual shift of ν_G from ~1585 to ~1580 cm^{-1} and ν_D from ~1350 to ≈1360 cm^{-1}; and c) initial narrowing of the symmetrical G' with shift of $\nu_{G'}$ from ~2695 to ≳2715 cm^{-1} followed by increasing assymmetry and broadening of this band culminating in the modulation characteristic of graphite.

Fig. 1 shows the width of the G band (including D') as a function of HTT for E (solid) and F (open symbols) surfaces. Widths ≲ 40 cm^{-1} indicate loss of D'; widths ≲ 25 cm^{-1} correspond to interlayer
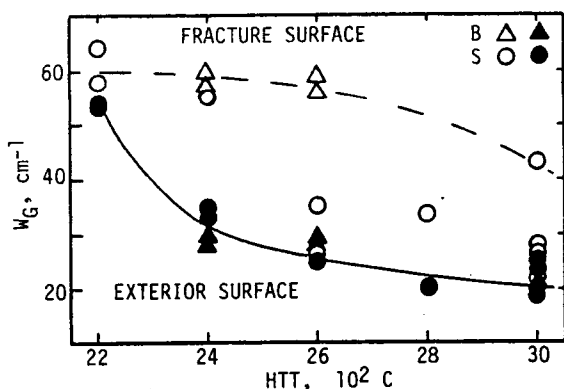
Fig. 1. Width of G (at $\approx 1580\,cm^{-1}$) versus heat treatment temperature for Beckwith and Sigri GLCs.

spacings $d_{002} \leq 0.342$ nm [12]. The ratio of the intensity of D to that of the combined G+D' bands is plotted in Fig. 2. Both of these figures show that the E surface is already less disordered than the interior (F) for HTT = 2200 C, and the 2-dimensional structure of the E surfaces develops rapidly as HTT increases to 2600 C. The scatter of the F results for HTT $\gtrsim$ 2600 C can be attributed to the fact that cracks developed in the samples during treatment so that the F surfaces obtained by crushing were a mixture of fresh interior surfaces and heat treated surfaces [6], which were indistinguishable in appearance. The interior structure is best represented by the most disordered F spectra. The results suggest that interior fracture data were not obtained for all samples.

The complete range of structural evolution, including development of 3-dimensional graphite crystallinity, may be monitored in terms of the evolution of the G' band by plotting $W_{G'}/W_G$ versus W_G as shown in Fig. 3, a modified version of a graphitization diagram proposed by Lespade et al. [12]. The lower limb of this plot corresponds to very disordered structures with $d_{002} \gtrsim 0.344$ nm; broad, assymmetrical G with appreciable D' intensity; and
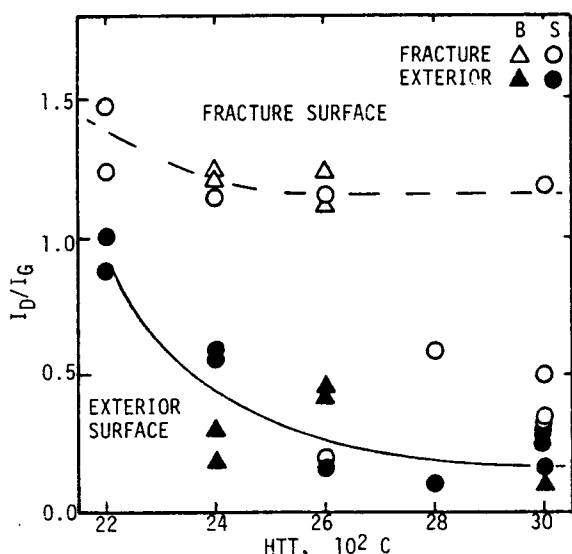

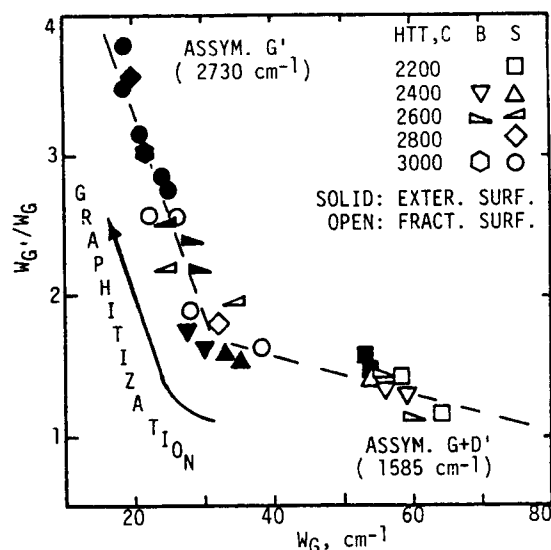Fig. 2 Relative intensity of D ($\approx 1350\,cm^{-1}$) versus heat treatment temperature.

Fig.3. Graphitization diagram based on evolution of the G' ($\gtrsim 2700\ cm^{-1}$) and G band widths.

symmetrical G'. The rising limb below the knee indicates graphitization with d_{002} decreasing toward the graphite value as W_G falls below $\sim 30\ cm^{-1}$, and $W_{G'}$ increasing as the doublet evolves with developing stacking order. The GLC data progress monotonically along this curve with increasing HTT, and the exterior (E) surfaces are always better graphitized than the fracture (F) surfaces of the same sample. The highest $W_{G'}/W_G$ values, those for Sigri E surfaces with HTT $\gtrsim$ 2800 C, correspond to modulated G' bands and approach the values found for well graphitized "soft" carbons [12].

Conclusions

These microprobe Raman results show that the exterior surfaces of monolithic glass-like carbons do indeed develop well-graphitized structures at high temperatures. This surface graphitization evolves progressively and apparently uniformly with increasing HTT $\gtrsim$ 2200 C, in contrast to the discontinuous, multiphase transformation that is characteristic of hard-carbon powders [9].

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