A solution for an accurate structural characterization of graphitized carbons on polished sections by Raman microspectrometry

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Introduction

Raman microspectrometry becomes nowadays a method of choice to characterize carbon materials. It is indeed one of the few techniques the most sensitive to the full range of the structural states present in this class of materials, from perfectly crystalline to amorphous. The first order region (1000-1900 cm^{-1}) of the single crystal of graphite exhibits only one vibrational band (called G band) located at approximately 1581 cm^{-1}. Additional bands appear whenever structural defects are created, crystallites size is reduced or graphene planes are bent. These bands are called "defect" bands: D_1 (~1350 cm^{-1}) and D_2 (~1620 cm^{-1}) [2-3]. Tuinstra & Koenig have proposed in 1970 an empirical law, usually used, which shows a linear relationship between the intensity ratio of D_1 band relative to G band and the coherent domain diameter ('crystallites size') L_a, determined by X ray diffraction [1]. However, one of the main problems of this calibration (established for non altered–surface of graphitised carbon) is the sensitivity of D bands intensity to the state of the analysed surface. Several authors have raised this problem to the sample preparation such as polishing, crushing or etching, insuring that this kind of the sample making greatly reduces the size of graphite crystals as a consequence of the growth of high D_1 band [4-6]. This could induce prohibitory errors in the structural characterization with an important consequence on the determination of the intrinsic degree of disorder as well as the properties governed by such ratio. However, to be able to detect different carbon components among others (carbon-carbon composites for aeronautic, electrodes or nuclear applications) or among silicates and metallic phases in natural and extraterrestrial carbons as meteorites [7], the polishing process is necessarily required (e.g. for an optical microscopy examination).

Experimental

The materials used are: a reference natural graphite (Ceylon (Sri Lanka)) and a series of graphitized carbon materials, produced by the pyrolysis of an anthracene-based coke at 1600, 2000 and 2900 °C [8]. Millimeter-sized grains of anthracene-based carbons were embedded in an epoxy resin and polished using 6, 3 and 1 µm diamond pastes to obtain several surface states. The characterization of the polished and unpolished carbon sections was performed by Raman microspectroscopy (InVia Renishaw). The spectra were collected under microscope (x50 objective) using the 514.5 nm wavelength [2]. The deconvolution of Raman spectra is obtained by the conventional fitting procedures, using Wire 2.0 program (Renishaw), so as to extract quantitative data. The output parameters are the band position, intensity, full-width at half maximum (FWHM) and integrated area of all the bands (D_1, D_2, D_3 and G).
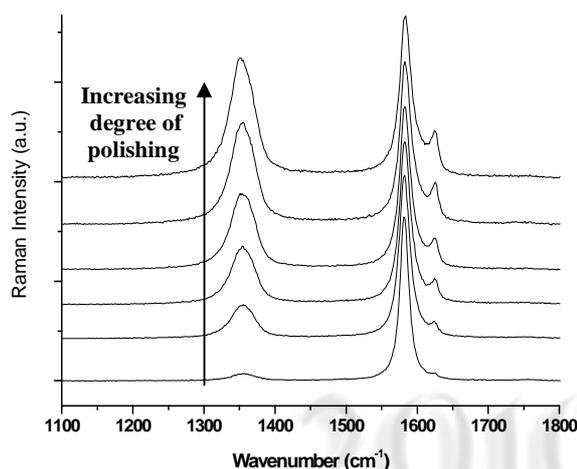

Fig 1 Different Raman spectra of an anthracene based-coke heated at 2900°C, corresponding each to varying polishing stages.

Figure 1 presents different Raman spectra of the anthracene based-coke heated at 2900°C, corresponding all to a highly graphitized carbon [8]. The reference spectrum prior the polishing process is shown at the bottom. The samples have been then subjected to an increasing degree of polishing stages (spectra from the bottom to the top) using diamond pastes with smaller and smaller grain size. For a better clarity, all the spectra were normalized with regard to the G band. Qualitatively, it appears clearly a high increase of D_1 and D_2 bands relative to G band, whereas G band width seems to be practically unchanged.

For the quantitative aspect, figure 2 presents the FWHM of G band versus the intensity ratio of D_1 band relative to G band. Firstly, a linear relationship between these two parameters, in the graphitization temperature range, is observed. At 2900°C, the graphite structure of anthracene-based carbon was achieved ($\frac{I_{D_1}}{I_G} < 0.05$; FWHM$_G$ < 17 cm^{-1}).

The correlation insures that the G band width, which is purely related to the crystal vibration, appears obviously as a reliable parameter to examine the disorder degree of the graphitized carbon materials, as the usual intensity ratio. This correlation is described by the linear function shown in figure 2.
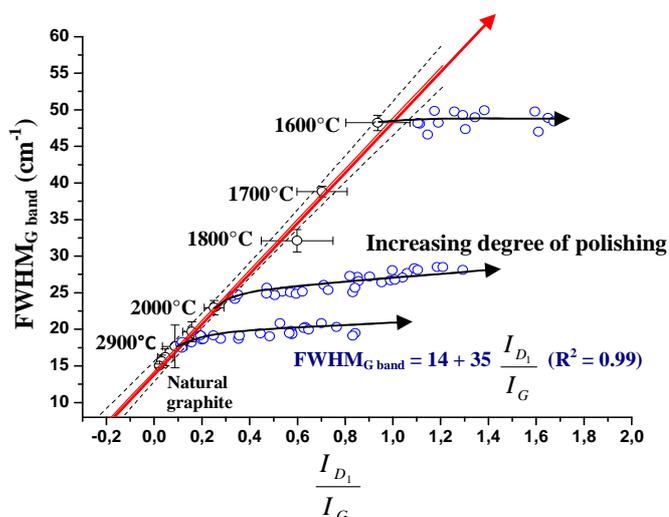
Fig 2 The evolution of G band width at half maximum versus the intensity ratio of D_1 band relative to G band of polished and unpolished graphitized carbons.

Our results also show that while the intensity ratio significantly increases with increasing the polishing degree, the G band width appears to be insensitive to this preparation process. Moreover, it is worthy to note that the polishing effect is less significant for non graphitized carbons obtained at 1600°C. In the contrary of what several authors could claim regarding the damage created in carbon materials upon polishing, this process clearly creates only very low structural disorder (the G band width varied only from 16.2 ±1.2 to 20.3, even if the ratio rises from 0.04±0.03 to 0.76), at least at the atomic scale. Besides, there is no reason, in the vibrational point of view, that a polishing of only few tens of minutes could create disorder as intense as what is suggested by the intensity ratio increase. Salver-Disma et al. have already demonstrated that a drastic mechanical milling has a real effect on carbon materials structure (as followed by XRD and HRTEM) after several hours **[9]**.

Conclusion

This work assesses the artefacts occurring during the polishing process of graphitized carbons. The intensity ratio, which is largely used up to now, appears to be particularly sensitive to the surface preparation of the graphitic samples, and provides consequently wrong information about the intrinsic structural disorder. This ratio must be avoided, at least for the most graphitized carbons. In contrast, the G band width appears to be much less sensitive to the preparation

making and therefore we highly recommend the use of this reliable parameter.

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