NEW DATA ON GRAPHTIZATION UNDER PRESSURE

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Introduction

The aim of this work is to study the mechanisms of formation of graphite under pressure at moderate temperatures from various organic precursors. Indeed, the synthesis of graphite in industry requires two conditions: an high temperature (about 3000°C) and a graphitizable precursor (a soft carbon characterized by a lamellar microtexture). In the natural process, graphite occurs under the effect of the metamorphism, at temperatures as low as 500°C, even with thermally non-graphitizable precursors (hard carbons), as microporous coals and anthracites. In this process, pressure (up to 10 GPa) and time (up to several tens of millions of years) are probably important parameters to take into account to explain the formation of natural graphite. The respective effects of temperature, pressure and strains are thus hardly discussed to explain the formation of graphite in natural and experimental processes. Inagaki and Naka, 1975 obtained graphite from non graphitizable precursors above 1600°C and at 0.5 GPa using a piston-cylinder like apparatus [1]. Bustin et al., 1995 lowered the temperature of graphite occurrence by the pyrolysis of an anthracite under pressure up to 1 GPa with a shear component [2]. In these works, the pressures are always moderate (< 1 GPa) and the experiment durations are short (usually smaller than 1 hour). In the present study, the effect of higher pressures (up to 8 GPa) and relatively long times (600 hours) were tested on experiments carried out at moderate temperatures (< 1000°C). We chose reference precursors, for which the behaviour versus temperature of treatment is already well-known [3]: a graphitizable carbon and a thermally non-graphitizable one. These precursors were heated up at 600, 800 and 1000°C under different quasi-hydrostatic pressures from 0.1 MPa up to 8 GPa during different duration of experiment from 5 to 600 hours. The structural and microtextural evolutions of products were characterized by coupling Raman microspectroscopy and High Resolution Transmission Electron Microscopy (HRTEM).

Experimental

Experimental runs were performed using an internal heated apparatus (IHA) for pressures below 1 Gpa and at higher pressures (1-4 Gpa) using a piston-cylinder apparatus (PCA). These apparatus allow to reach temperatures of 1000°C and to use, during the same experiment, 2 or 3 wedged capsules (about 10 mg sample per capsule) in argon atmosphere. In these experiments as NaCl (PCA) and Argon (IHA) are used as pressure transmitting medium, pressure is supposed to be quasi-hydrostatic. At last, in order to reach higher pressure (8GPa / 1000°C), we used a multi-anvil apparatus in which pressure can also be considered as quasi-hydrostatic.

A graphitizable lamellar carbon (an anthracene-based semi-coke) and a thermally non-graphitizable microporous carbon (a saccharose-based coke) were chosen as precursors. The evolution of the multiscale organisation (structure and microtexture) of so-obtained products was characterized by coupling Raman microspectroscopy and TEM modes.

Structure and microtexture of carbon materials can be directly imaged using TEM by coupling various modes [3,4]. HRTEM investigations were performed using a Philips CM20 microscope working at 200 kV, giving a resolution of 0.144 nm in lattice fringes. In this study, we mainly used high-resolution mode with magnification about 300,000 , and bright-field (BF) and dark-field (DF) modes with magnification about 50,000 . Thanks to the 002 lattice fringe technique (002 LF), it is possible to image directly the profile of the aromatic layers. Moreover, by coupling high-resolution mode with low-magnification BF and DF images, TEM is useful to specify the sample heterogeneity at the nanometre scale whereas Raman spectroscopy or XRD give average information by sampling volumes of a few µm and mm, respectively. We have coupled these images with selected-area electron diffraction patterns (SAED) to specify the crystallinity range of the sample and especially to follow the occurrence of the triperiodic order. These
SAED were obtained on volumes less than 1 µm in diameter and 0.1 µm in thickness.

We used a Dilor XY double subtractive spectrograph with premonochromator, equipped with confocal optics before the spectrometer entrance, and a nitrogen-cooled EGG CCD detector. A microscope is used to focus the excitation laser beam (514.5 nm exciting line of a Spectra Physics Ar⁺ laser) on the sample and to collect the Raman signal in the backscattered direction. The presence of the confocal pinhole before the spectrometer entrance ensures a sampling of a 2-4 µm sized zone with a 50 µm objective with a final laser power about 1-15 mW on the sample. Acquisition of 20-300 seconds have been made and 10-20 spectra were recorded for each sample. Peak positions, peak areas (i.e. integrated area) and peak width (i.e. full width at half maximum, FWHM) were determined using computer program PeakFit 3.0 (Jandel Scientific). In the first order region of the spectrum (1100-1900 cm⁻¹), the relative area and intensity of the defect band (1350 cm⁻¹) are reliable parameters to characterize the degree of organization of carbonaceous material [4]. It can be completed by the informations from the second order region (2400-3300 cm⁻¹) such as the splitting of the 2700 cm⁻¹ band with the apparition of the triperiodic order and the relative area of the 2900 cm⁻¹ which is also a good indicator of the degree of organization.

Results

All the precursors are made of polyaromatic layers frequently stacked by 2 or 3 to form Basic Structural Units (BSU) of nanometric size. The 002 LF image show the lamellar microtexture of the anthracene-based semi-coke, due to the preferential planar orientation of the BSU (see Figure 1a), responsible for their subsequent graphitisability. By contrast, the saccharose-based coke exhibit a microporous microtexture, due to the strong misorientation of the BSU (see Figure 2a), preventing its thermal graphitisability.

A preliminary serie of experiments was performed in order to specify the effect of the low temperatures (<1000°C) applied during a moderate duration fixed at 95 hours. In these conditions, we did not observed structural modifications of the microporous precursor whereas the structural organisation of the lamellar one was significantly modified. In fact, the length of the aromatic length and the number of stacked layers weakly increases at 2 GPa/800°C; the so-obtained carbon becomes equivalent to an anthracene-based coke heat-treated at 1300-1500°C under ambient pressure.

We have then focused on a temperature of 1000°C and different values for both pressure and time. In fact, at 1000°C the graphitization is strongly enhanced by hydrostatic pressure for the both types of precursors. More organised phases and graphite are detected by HRTEM (see Figure 1c and 2d), whereas the intensities of the Raman defects bands are considerably lower in high-pressure samples compared to 0.1 MPa experiments performed at the same temperature (see Figure 4). Moreover, the HRTEM images shows that the homogeneous precursors submitted to pressure systematically lead to structurally and microtexturally heterogeneous carbons, especially with microporous precursors where poorly modified coke up can be mixed with graphite. Nevertheless, triperiodic graphite was detected by electron diffraction within all precursors synthetized at 1000°C and 2.0 Gpa.

In order to specify the pressure effect, we first focused on the graphitization mechanism observed for a given temperature fixed at 1000°C We performed experiments at 0.1 MPa, 0.1 GPa, 0.5 GPa, 2 GPa and for 4 GPa during the same duration (95 hours). In the case of the anthracene-based coke, the graphitization is more complete as pressure increases, without microtextural changes: the microtexture remains lamellar whatever the pressure applied (Figure 1). The mechanism is the same as the one classically described for a 0.1 Mpa pressure [3]: improvement of the parallelism and in-plane growth of the aromatic layers.

By contrast, for microporous precursors (non-graphitisable under the only effect of temperature), pressure allows their graphitization. It is made possible only by microtextural changes. In the case of pressures lower or equal to 4 Gpa, graphite is observed within larger and larger pore [5]. Under the pressure effect, the pore diameter increases and we observed a succession of microtextures between the starting microporous material, a mesoporous carbon, and a macroporous one which occurs between 0.1 et 0.5 GPa. At these intermediate pressures, the products are made of a mixture of partially glassitised macroporous carbon and of the microporous turbostratic starting coke as shown by the figure 3.
Figure 3. HRTEM images of a anthracene-based semi-coke treated at 1000°C during 95 hours, and with an applied pressure of 0.1 GPa (a), 0.5 GPa (b) and 2 GPa (c).

Figure 3. HRTEM image of a saccharose-based coke treated at 1000°C, during 95 hours, and with an applied pressure of 0.1 MPa (a), 0.1 GPa (b), 0.5 GPa (c) and 2 GPa (d).
These transformations microporous – mesoporous - macroporous carbons are enhanced with increasing pressures. Such microtextural changes allow a structural improvement : the length of the aromatic layers and the number of stacked planes increase. The transition macroporous - lamellar carbons permits the formation of large layers (Figure 2c-2d), stacked in the A-B sequence characteristic of graphite crystals (as attested by the $hkl$ reflections present in the SEAD patterns). At higher pressures (2 and 4 GPa), some well cristallized graphite locally occurs, whereas a lot of microporous starting material are still present, the macroporous phase being rare. The 8Gpa, 1000°C is only made of small graphite flakes with remnants of weakly transformed microporous carbon.

The Raman data well agree with the HRTEM results and allow a more quantitative global quantification of these graphitization processes. However, the heterogeneity observed in the HRTEM investigations, remain detectable at the Raman scale. About 10 spectra per sample were recorded. However, in the following figures, for a better clarity, we chose to illustrate the evolution with the spectra representative of the most evolved part of the sample. For the both precursors, the intensity of the defect band at about 1350 cm$^{-1}$ decreases and the $E_{2g}$ band at 1580 cm$^{-1}$ remains the only visible band from a pressure of 4 Gpa (Figure 4a). The latter becomes narrower and narrower as the graphite proportion (imaged by HRTEM) increases. Such evolutions correspond to the progressive structural improvement made possible by the release first of the heteroatoms (hydrogens, oxygens), then by different types of defects placed outside and within the aromatic layers [4]. This evolution is confirmed in the 2$^{nd}$ order mode, by the progressive disappearance of the 2900 cm$^{-1}$ defect band (Figure 4b), the occurrence of the triperiodic order being shown by a beginning of splitting of the 2700 cm$^{-1}$ graphite band when $hkl$ reflections develop in the DEAS patterns. The graphitization process appears more rapidly and more completely with the anthracene-based semi-coke, i.e. with a thermally graphitizable precursor.
A second series of experiment was carried out during different durations (1, 5, 95, 240, and 580 hours) at 1000°C and 0.5 GPa. If the precursors are only weakly modified after 5 hours experiments, they are strongly transformed into graphite after 580 hours. This shows a strong kinetic control on the graphitisation processes, with all precursors.

Conclusion

With all synthetic precursors, whatever their pristine microtexture, graphitization is enhanced by hydrostatic pressure by comparison with the purely thermal process. However, the mechanisms appear strongly different according to the microtexture of the precursor. The lamellar carbons remain lamellar, whereas striking microtextural changes are required to permit structural improvements and the occurrence of the triperiodical order of the graphite. All the mechanisms are controlled by the kinetics. We are trying now to quantify this by Raman microspectroscopy. This assumption could explain that, at the geological timescale, graphite commonly occurs at a temperature of 500°C. Using the same analytical approach, applications are developed in the earth sciences field (characterization of the degree of metamorphism). We are studying natural samples (coals and kerogens) metamorphosed under various geothermal gradient (Western Alps (300-800°C, 0.5-4 GPa), Central Alps (400-650°C, 0.1-5 GPa) and Japan (350°C-600°C, 0.5-1.8 GPa)). In these natural samples, as observed by HRTEM, graphitization process follow a mechanism very similar to the one shown for the saccharose-based cokes submitted to a pyrolysis under pressure [6]. Such graphitization seems mainly controlled by temperature; the decrease of the 1350 cm\(^{-1}\) Raman band appears as an efficient paleothermometer [7].

References


Figure 4. Evolution of the Raman spectra versus the applied pressure (temperature of treatment: 1000°C, duration: 95 hours). Example of the anthracene-based semi-coke. a: first order spectra; b: second order spectra.