

FROM DISORDERED CARBONS TO GRAPHITE: A HETEROATOM CONTRIBUTION

Sylvie Bonnamy, CRMD, CNRS-University, 1B rue de la Ferrollerie, 45071 Orleans cedex 2, France

Agnès Oberlin, CNRS, Mas Andrieu, 34380 Argelliers, France

Abstract

Many carbonaceous substances derive from natural or industrial precursors coalified or carbonized in plastic condensed phase. To understand their behaviour during carbonization and graphitization, it is necessary to associate crystallographical and physico-chemical data. Indeed, the elemental composition of the precursors (C,H,O,N,S) is extremely variable. The heteroatom content may reach more than 35 wt% in the initial material and is often still noticeable well above 1000°C (5-10 wt%).

Examples taken among oil products, coals, pitches, ... will illustrate the fact that the maximum degree of graphitization (d_{002} minimum, P_1 maximum) measured at 2800°C is directly connected to the heteroatom content measured at the liquid crystal phase occurrence. The numerical parameter to take into account is the atomic ratio of cross-linking atoms (O,S) versus hydrogen which plays a solvolytic role as suspensive medium during primary carbonization. This parameter will govern the evolution of such materials during their thermal treatment and the future end-products properties.

Keywords: carbon precursor, carbonization, graphitization, disordered carbons, heteroatoms, crystallography, physico-chemistry

Introduction

The formation of carbonaceous substances, their evolution to pure carbon (carbonization) and eventually their graphitization are particularly complex (Oberlin, 1984; Oberlin et al., 1989). Therefore, almost any kind of disorder is found from amorphous (zero dimensional order or 0D), to turbostratic (2D order), then crystalline final order (3D order) (Oberlin et al., 2006).

Carbonaceous matter, i.e. the so-called disordered carbons, is not transformed into pure carbon before 2000°C. Pure carbons are never found in nature except natural graphite. The persistence of heteroatoms (such as oxygen, sulfur, nitrogen and hydrogen) fixed by chemical bonds on the edges of aromatic molecules limit their size and the interactions between them. The history of heteroatom release is the key to well understand the different events occurring during primary and secondary carbonization (softening, liquid crystals demixtion, solidification and polygonization) (Oberlin et al., 1999; Bonnamy, 1999). During graphitization, the impact of the precursor heteroatoms is the production without gap of intermediates (partially graphitized) between non graphitizing and graphitizing carbons. We will demonstrate, that there is a continuous series from disordered material to graphite expressing the diversity of the precursors elemental compositions (Oberlin and Bonnamy, 2007).

Experimental

To illustrate the purpose of our paper, examples of evolution of carbon materials during carbonization and graphitization will be taken among samples derived from natural and industrial precursors, i.e coals, polymers (resins,..), kerogens (parent rock of oils), pitches, refinery residues, CVD carbon films, model substances,..).

The carbonization treatments done up to 1000°C are performed at a 4°C.min⁻¹ heating rate. As for the graphitization treatments, they are performed at a 20°C.min⁻¹ heating rate.

The main characterization techniques used are TEM imaging (Bright-field, 002 Lattice fringes, hkl Dark Field modes) and diffracting techniques (X-ray diffraction, electron diffraction), joined to physico-chemical ones such as chemical analysis, IRFT ESR, Vickers microhardness,...

Events characteristic of primary carbonization

Except in gaseous phase (not presented here), carbons derive mostly from thermal conversion of macromolecules (or polymers) handled by nature from biomass (coalification) or by industry from oil or coal heavy derivatives (carbonization). The elemental composition of the precursors (C,H,O,N,S) is extremely variable and it changes more or less rapidly as coalification or carbonization progress (Oberlin et al., 1980; Oberlin, 1989; Oberlin et al., 1999).

Carbonization (as coalification) begins by the softening of the precursors. It breaks into smaller molecules and forms a suspension more or less viscous. The heaviest molecular fragments or Basic Structural Units (molecular masses 600 – 900 amu) are dispersed into the lightest (200 – 300 amu) (Oberlin, 1984; 1989) acting as suspensive medium (van Krevelen, 1981, 1993). The latter are mainly hydrogenated species. As heteroatoms release and as volatiles become increasingly lighter, the hydrocarbons are produced with an increasing rate. At the maximum rate, the concentrated suspension provides demixtion of liquid crystals (mesophases or Local Molecular Orientation). This sudden occurrence of LMO's is expressed as the sudden production of 002 reflections in the X-ray patterns. Between liquid crystals demixtion and solidification, the mesophases grow by coalescence into mosaics. Viscosity and Vickers microhardness increase up to infinity. At solidification, primary carbonization is over.

Considering hydrogen poor and oxygen rich samples up to hydrogen rich and oxygen poor ones:

- The softening point decreases
- The sudden LMO occurrence (demixtion of mesophases) ranges between 460 and 470°C for a carbon percentage between 84-90 wt% C for all samples.
- The solidification point increases from 460°C up to 510°C, it corresponds systematically to a constant value of $H/C_{at} = 0.5$
- Between LMO occurrence and solidification, LMO's grow by coalescence up to 100% anisotropy.

However, tentatives to include the heteroatoms contribution in the crystallographical calculus or at least in texture and structure evaluations began with studies on coals (Diamond, 1958; Ergun, 1968).

Secondary carbonization

At solidification, the pure carbon step is not yet reached. For example, in the case of kerogens the range is 85-90 wt%C (Oberlin et al., 1980) and in the case of coals 92 wt%C for coals (van Krevelen, 1981;1993). The release of residual heteroatoms (gases) carries-on progressively down to zero, the end of secondary carbonization.

During secondary carbonization, BSU's become increasingly coherent by free radicals recombination. In 002 lattice fringes images, long distorted layers are associated in turbostratic stacks (diameter L_a) containing N layers. N and L_c increase moderately up to 1500-1600°C. Then, after a sudden change of slope, N_{max} ceases to be measurable above 1900°C at $N = 30$. L_a stays between 30 and 200 Å up to 2000°C, then increases fastly up to 1000 Å at 2300°C, above which it cannot be measured. From 2000°C, 11 dark-field takes over the measurement of L_a (Oberlin, 1984). Most of the techniques preceedingly used for characterization become rapidly useless. Fortunately, there is some kind of "magic temperature" (about 2000°C), where all electronic properties show a sudden accident.

The final explanation of polygonization is given by the jump in activation energy occurring simultaneously: polygonization is the sudden wiping-out of all residual intralayer defects (Pacault, 1965; Fischbach, 1971).

In the same manner, as various LMO's are the consequence of the elemental composition of the precursor, the future behaviour of the final pure carbon, will depend on the LMO size. The heteroatoms initially present remain the thread, which leads carbonization toward graphitization(Oberlin and Bonnamy, 2007).

Graphitization as a consequence of the precursor elemental composition

Above the 2000°C, P_1 (the probability to find a pair of graphenes having the graphite AB sequence) becomes measurable (Maire and Méring, 1970; Iwashita and Inagaki, 1993) and increases rapidly (the inflection point in the curve P_1 versus HTT occurs systematically between 2000 and 2200°C. Numerical values of the graphitization degree (P_1) are thus obtained only by calculus of the successive profiles of the 11 band of the X-Ray patterns (Warren, 1941; Franklin, 1951, Maire and Méring, 1970, Iwashita and Inagaki, 1993; Rannou et al, 1994). It varies between zero (for non graphitizing carbons) up to 1 for natural graphite. It is near 0.75 - 0.80 to almost 0.90 for the best graphitizing carbons.

Intermediate samples (partially graphitized) (Oberlin, 1989; Oberlin et al, 2001; 2006, 2007)

In fine, the consequence of the precursor heteroatoms on the end-product at $HTT \geq 2800^\circ\text{C}$ is the production of intermediates between the non-graphitized carbons ($P_1 = 0$, or < 0.1) and the highly graphitized materials ($P_1 \geq 0.75$).

As P_1 increases, F_{LMO} decreases and LMO sizes increases. This signifies that it is mainly the persistence of an increasing amount of cross-linkers, which increasingly limits the maximum value of graphitization (Figure 1).

Obviously, there is a continuous series travelling all along the various precursors and their end products without any accident.

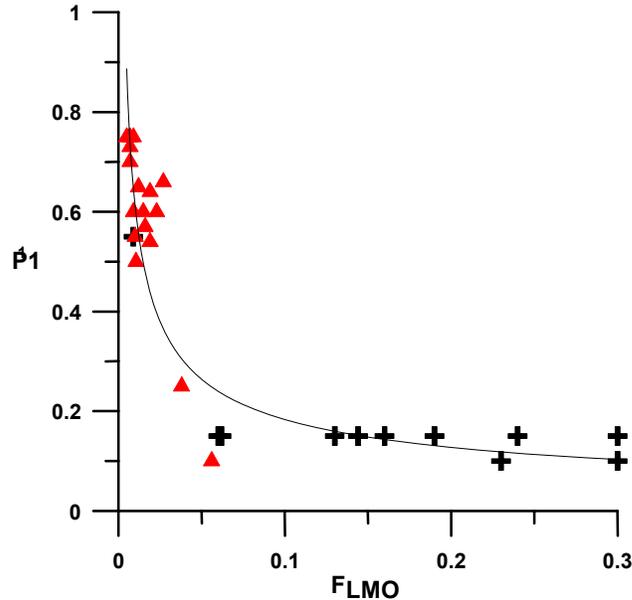


Figure 1. Example of correlation between P_1 (graphitization degree) and the presence of heteroatoms. F_{LMO} is the ratio $(O+S)/H$ measured at liquid crystals occurrence during primary carbonization.

Conclusion

This paper leads to be conscious that the heteroatom content of carbon precursors is the leading parameter which governs the future end-product properties, whether mechanical (fragile or ductile), thermal (insulator or not), electrical (conductor or not), etc.

To understand the behaviour of series of unknown products, it is compulsory to combine physico-chemical and crystallographical techniques, since they are complementary.

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