

POSSIBLE ROLE OF IRON IN GRAPHITE FORMATION

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INTRODUCTION

The classical way of obtaining graphite consists in heating lamellar cokes to 2800°C in absence of oxygen. These cokes are composed of large domains, within which the polyaromatic Basic Structural Units (BSU) are oriented in parallel over a few micrometers. Graphite is reached by a progressive improvement of the order, followed by the coalescence of the BSU and crystal growth [1]. At the opposite, cokes made of small domains (less than 10 nm) are not thermally graphitizable and give porous turbostratic carbons. Anthracene-based chars and saccharose-based chars are respectively frequently used as standards of graphitizable and non-graphitizable carbons [1].

Graphite can be obtained through other mechanisms, at temperatures lower than 2000°C. Saccharose-chars can be transformed below 1800°C, in the presence of small amounts of molten iron (< 10 %), into turbostratic hollow spherules of carbon, mixed with graphite flakes [2]. These phases were attributed to the respective decomposition of unstable iron carbides, such as cementite Fe₃C, and of a solid solution of carbon in iron, with a composition supposed to be close to Fe₃C [2]. In similar conditions, i.e. in the presence of molten iron, well-crystallized graphite can be obtained from iron-carbon melts [3], similar to the "Kish" graphite met in blast furnace metallurgy. The formation of this Kish graphite was attributed to precipitation, during cooling, from carbon-saturated iron melts [4].

In the present work, we chose to try to synthesize graphite in conditions similar to those indicated above (in the presence of iron, and at temperatures below 2000°C) and thus very different to the ones required for the classical progressive graphitization of graphitizable carbons.

EXPERIMENTAL

Two types of carbons were used as precursors : the anthracene-based chars (AC) and the saccharose-based chars (SC) respectively chosen as examples of graphitizable and of non-graphitizable carbons. Two forms of iron were tested : a powder of metallic iron (Fe) and a powder of iron oxide (Fe₂O₃). Different blends were prepared containing about 10, 25 and 50 % in weight of iron, i.e. in proportions too high to allow pure catalytic mechanisms but in which carbon was in sufficient excess to obtain stoichiometric cementite (for which 6.7% carbon are required). These blends were heat-treated under an argon flow to 1150°C (temperature below the carbon-iron eutectic, i.e. 1153°C), 1600°C (temperature above the melting point of pure iron, i.e. 1536°C) and 2000°C. The conditions of treatment were : heating rate : 20°C.min⁻¹, and 15 minutes residence time at the Highest Temperature of Treatment (HTT).

Characterization of the carbons obtained under these conditions was mainly performed by X ray Diffraction (XRD), by studying the evolution of the 002 peak due to the diffraction on the aromatic planes.

Moreover, a Transmission Electron Microscopy (TEM) characterization is currently under way, especially by the bright field mode in order to visualize the porous or lamellar morphologies, and by selected area electron diffraction (SEAD) allowing local structural characterization [1,5].

RESULTS

The diffractograms of the carbons obtained from the ex-saccharose (SC) and the ex-anthracene chars (AC) heat-treated in absence of iron between 1150 and 2000°C show a single broad 002 reflection; the corresponding mean interlayer spacings d_{002} decrease from 3.75 to 3.55 Å for SC, and from 3.5 to 3.42 Å for AC. In contrast, the diffractograms of all the carbons obtained from iron-carbon blends heated above 1600°C contains two distinct 002 lines (Figure 1). As the maxima of these reflections are distinct, the experimental 002 line was easily decomposed by computer into two peaks.

The first 002 peak ($d_{002} = 3.40\text{-}3.50$ Å) corresponds to yet turbostratic carbons. The second, placed at the larger angle, leads to d_{002} less than or equal to 3.36 Å; this position is very near of the one obtained with Ceylon graphite ($d_{002} = 3.354$ Å) and consequently significantly lower than the values reached by graphitizable carbons heated at high temperatures (the d_{002} of the anthracene char heated at 2800°C is 3.361 Å).

The presence of graphite *sensu stricto* appearing at temperatures much lower than the 2800°C required for the usual progressive graphitization is also confirmed by the first results of TEM study. The bright field images bring out the presence of large flat lamellae (micrograph of Figure 2) with SAED patterns characteristic of graphite.

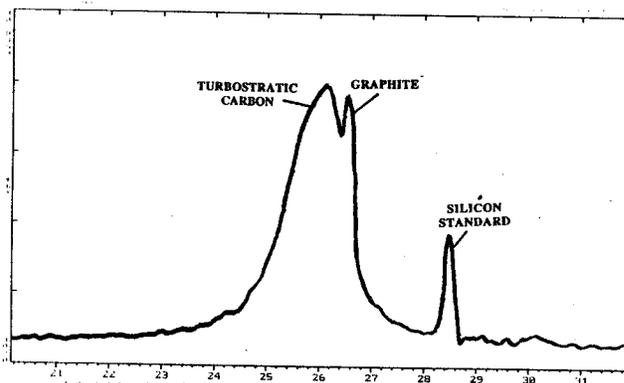


Fig. 1. Diffractogram of carbon-iron blends heated above 1600°C : graphite phase coexisting with a still turbostratic carbon phase.

From S, the ratio of the area of the 002 graphite peak to the area of the total composite 002 peak, the proportions of graphite in the different carbon samples can be estimated and the respective effects of the heat-treatment temperature and of the nature of the iron introduced in the blend can be studied (Table).

Sample	d ₀₀₂ (Å) peak 1	d ₀₀₂ (Å) peak 2	S %
AC + 29% Fe 2000°C	3.424	3.358	18.2
AC + 50% Fe 2000°C	3.417	3.359	51.5
SC + 23% Fe 2000°C	3.402	3.363	22.8
SC + 50% Fe 2000°C	-	3.354	100
AC + 18% Fe 1600°C	3.442	3.360	8.7
AC + 50% Fe 1600°C	3.420	3.358	45.5
SC + 20% Fe 1600°C	3.496	3.375	11.0

Table. X-ray diffraction data on carbons resulting of heat-treatment at 1600 and 2000°C of different iron-chars blends (AC: anthracene-based char previously heated at 1100°C; SC : saccharose-based char previously heated at 1000°C); mean interlayer spacing d_{002} and the ratio S.

The proportions of graphite in the carbon samples increase both with the temperature of treatment and the proportion of iron in the blend (Table). Moreover, the graphite is more easily obtained from the mesoporous saccharose-based char than from the lamellar anthracene-based char. At 2000°C, with 50 % iron in the blend, the transformation is nearly complete if saccharose char is used, whereas the ratio S remains about 1 with the anthracene-based char. No reliable difference was detected depending on the nature of the iron (Fe or Fe₂O₃) introduced in the blends : the positions and the ratios S of the peaks are similar if the proportion of Fe in Fe₂O₃ is taken in account.

The d_{002} value of the first peak, corresponding to a yet turbostratic phase, decreases from 1600 to 2000°C, especially in the case of the SC-based carbons for which the d_{002} values are significantly lower than the ones measured on SC-based carbons heated in this range (about 3.6 Å); this suggests that the saccharose char was strongly modified. At 2000°C, whatever the nature of the precursor, the d_{002} values are similar to those of the graphitizable chars heated at 2000°C in absence of iron, but also to the catalytic macroporous carbons [5]. In order to discriminate among the different turbostratic carbon phases (mesoporous, macroporous, lamellar) which could be present, TEM characterization was performed.

The SC-based blends are a mixture of graphite lamellae, macroporous carbons and remnants of non-transformed SC. The macroporous carbons are probably responsible for the first peak observed in the diffractograms, since the SEAD patterns performed on non-transformed SC give 002 rings too weak to be detectable in the X-ray diffractograms; The carbons from AC-based blends are very different from those of SC-based blends, since they are mainly composed of lamellar phases : graphite flakes with lamellar turbostratic non-transformed AC.

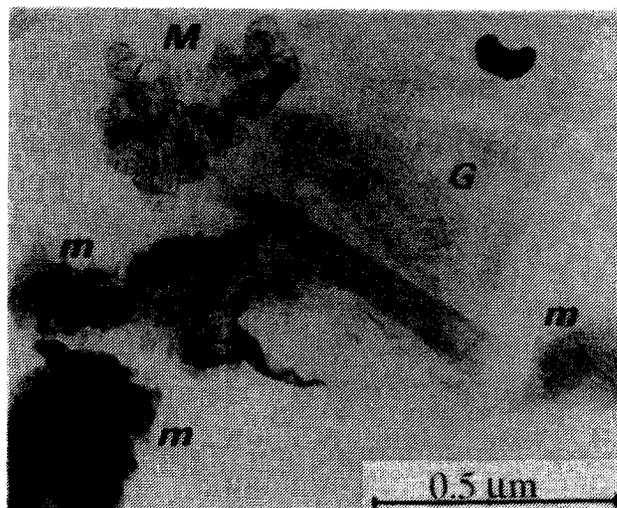


Figure 2. Bright-Field TEM image of a saccharose char heated at 1600°C with 50 weight % of Fe₂O₃ : G : graphite lamellae, M macroporous new phase, m : mesoporous non-transformed SC.

DISCUSSION - CONCLUSION

Graphite can be obtained from char-iron blends heated at 1600°C, i.e. above the melting point of iron. The graphite yield increases with the amount of iron in the blend and temperature, which favors carbon dissolution in the molten iron. Char microtexture appears to be an important parameter since the yield is higher with mesoporous (SC) than with lamellar (AC) chars. The transformation is nearly complete with SC-iron melts with 50 wt % Fe, heated at 2000°C.

The SC are more reactive towards iron than the AC since the proportion of free edges of aromatic layers is much higher; consequently, they can react more completely, and at lower temperatures. The macroporous carbon phase, appearing essentially in SC-based carbons, is quite similar to the catalytic carbon, previously described, and attributed to the decomposition of an unstable iron carbide [2,5].

The mechanism of formation of *stricto sensu* graphite probably involves a complete dissolution of the carbon in molten iron. When oversaturation is reached, graphite precipitation can occur, without the need of transition via a carbide.

Our results show that graphite becomes the main reaction product when both the amount of iron in the blends and the heat treatment temperature increase, i.e. when carbon dissolution in iron is favored. Quantitative TEM study, especially of samples from melts quenched at different temperatures, could lead to an understanding of the mechanisms involved in this formation of graphite.

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