NEW DATA ON ANTHRACITE GRAPHITIZIBILITY

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INTRODUCTION

Graphite is obtained by pure heat-treatment to 2800°C and in absence of oxygen, of cokes with lamellar microtexture, i.e. made of domains within which the polyaromatic Basic Structural Units (BSU) are oriented in parallel over a few micrometers. At the opposite, cokes made of domains smaller than a few tens nanometers only give porous turbostratic carbons [1,2]. However, if microporous precursors are mechanically strained along a plane during the carbonization stage, they acquire a "2D" microtexturation, i.e. the BSU become preferentially oriented along the plane; consequently their microtexture tends to become lamellar and graphitizable. Our previous studies [3,4] show that the higher the preferential planar orientation of the BSU in the char, the higher the graphitization degree of the carbon obtained after a simple thermal treatment at 2800°C. Such 2D microtextured carbons can be obtained especially when the carbonization stage is performed under anisotropic pressure [4].

Anthracites are naturally carbonified coals (%C > 90). They are chosen as raw materials in carbon materials manufacturing for several applications. For these applications, they must first be heat-treated from 1200°C to reduce their reactivity and to improve their electrical and thermal conductivities. These properties seem connected to the evolution, during the heat-treatment, of their porosity and their graphitization degree. As anthracites are mesoporous (pores < 200 Å), they should be non-graphitizable carbons. However, previous work [5,6,7] showed that if anthracites behave as non-graphitizable carbons up to 2000°C, they graphitize above this temperature, but by a different way as compared to classical thermal graphitization. This mode was attributed to the improvement of pore flattening, considered as characteristic of anthracites and assumed to be the result of stresses developped in Nature by lithostatic pressure or by tectonics. Our recent studies on anthracite graphitizability, performed by Transmission Electron Microscopy (TEM), showed that heat-treated anthracites are not always graphitizable [3,8]. They are a mixture of carbonaceous phases extending from isotropic porous turbostratic carbons to graphite lamellae, through more or less graphitized facies corresponding to more or less flattened pores. According to their origin, some anthracites lead, at 2800°C, to carbons mainly composed of graphite lamellae, whereas others give still porous and turbostratic carbons [3]. From these results, we assumed that the ability of anthracites to transform into graphite depends on the presence, in the raw anthracite, of preferential planar orientations of the BSU (2D microtexturation) probably due to the existence of flattened pores. The aim of the present work was to test this hypothesis by studying microtextural and structural evolutions of some anthracites during the treatment at 2800°C.

EXPERIMENTAL

Several anthracites, from different geographical and geological origins, were used. They were heat-treated, under an argon flow up to 2800°C (heating rate : 20°C.mn^{-1}, residence time at the highest temperature : 15 min).

Their subsequent structural and microtextural evolution was mainly followed by TEM [9] :

- selected area electron diffraction (SAED) allowing local structural characterization,
- bright field mode to image porous or lamellar morphologies, 002 lattice fringes technique to bring out the profile of the aromatic layers and,
- 002 dark field mode to have access, with a resolution better than 10Å, to material microtexture, i.e. to the mutual orientation in space of the BSU. By this mode, only the BSU of a given orientation appear bright and different types of preferential planar orientation, common in raw anthracites, can be brought out. The heat-treated samples being usually heterogeneous, they were semi-quantified with the help of histograms of microtexture (see figure 2).

RESULTS

The 002 dark field images show that the raw anthracites studied are poorly organized. They are composed of nanometric polyaromatic BSU, generally relatively misoriented and responsible for the globaly isotropic microtexture. However, weak preferential planar orientations of the BSU are detectable and are responsible for usually slightly anisotropic microtextures.

Four types of microtextures were met in the raw anthracites studied and are sketched in Fig. 1 :

- "1B" : the BSU are randomly distributed; this microtexture is characteristic of low rank coal which have not reached the semi-coke stage and which are usually still visco-elastic;
- "1A" : the BSU are locally oriented in parallel within domains (< 20 nm) which form pore wall; these porous microtexture is characteristic of thermally matured coal having reached naturally the semi-coke stage, i.e. the brittle solid stage (1);
- "2B" : the BSU exhibit a preferential planar orientation, similar to a flow anisotropy;
- "2A", corresponding to "classical" flattened pores [5,6,7].

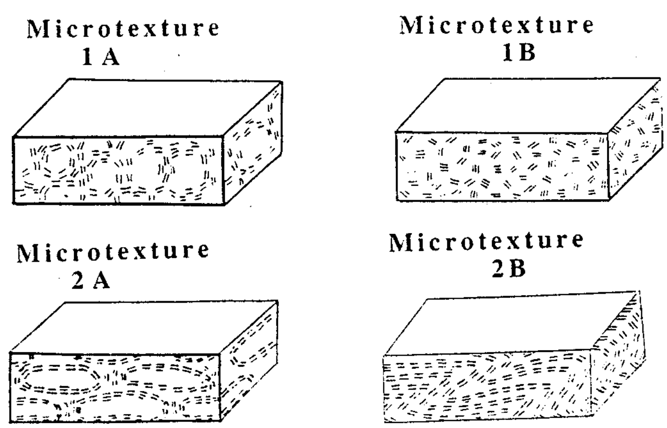

Fig. 1. Sketch of different microtextures in our raw anthracites.

When anthracites are heated to 1000°C, the "B" microtexture disappears and the anisotropy of the "2A" particules was strongly improved.

Important microtextural changes are observed in the samples heat-treated up to 2800°C, since more or less perfect lamellae are imaged besides more or less anisotropic porous carbons. Five types of microtexture were distinguished using the 002 dark field images : porous particles with isometric pores (type 1), particles with an increasing 2D microtexturation due to increasingly flattened pores (types 2 and 3), then lamellar microtextures : "imperfect" lamellae which still retained pore walls normal to the orientation plane (type 4) and *stricto sensu* lamellae (type 5); these microtextures are sketched in Figure 2; as the BSU coalesce before 2000°C, the aromatic planes profile was represented by a continuous line. The higher the 2D microtexturation in the raw anthracite, the more graphitized is the heat-treated anthracite.

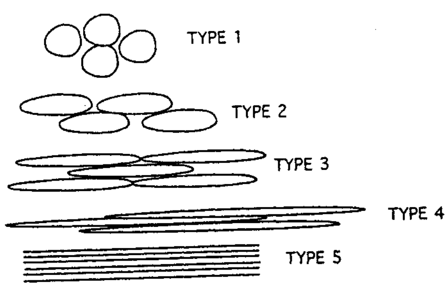

Fig. 2. Sketch of the different types of microtextures brought out in the heat-treated anthracites studied.

Heat treatment up to 2800°C leads to a shift toward lamellar microtextures (types 4 and 5). The SEAD patterns show that porous microtextures remain turbostratic, whereas the graphitization degree of the lamellae strongly increases from type 4 to type 5 (graphite *stricto sensu*). The stronger the 2D microtexturation of the raw anthracite (expressed by the 2A or 2B microtextures), the higher the amount of graphite at 2800°C. Two extreme behaviours are presented in Figure 3 : anthracite 1 being very isotropic ("1A" microtexture), it remains mainly porous and turbostratic at 2800°C and is consequently weakly graphitizable. In contrast, raw anthracite 2 contains anisotropic particles ("2A" in this case) and gives graphitized lamellae at 2800°C; it is strongly graphitizable.

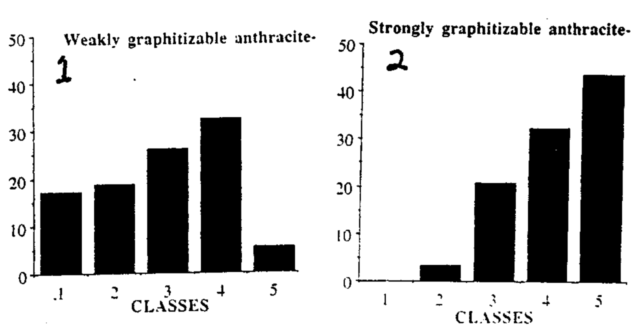

Fig. 3. Histograms of microtexture of weakly graphitizable and strongly graphitizable anthracites heated at 2800°C.

DISCUSSION-CONCLUSION

Our present results agree well with the hypothesis that the ability of anthracites to graphitize depends on the presence of a 2D microtexturation (preferential planar orientations of the polyaromatic BSU) in the raw anthracite, responsible for their subsequent at least partial graphitization.

According to the moment when the mechanical stresses are applied during natural carbonization (coalification), this microtexturation is expressed as flow microtexture (2B microtexture) or as flattened pores (2A microtexture). The microtextures 1A and 1B are isotropic and indicate the absence of anisotropic strains during the geological history; they differ however by their degree of thermal maturation, since the 1B microtexture corresponds to a weakly matured anthracite, whereas the 1A is characteristic of semi-cokes. The two microtextures 2B and 2A are anisotropic and reveal the existence of a stage during which the anthracite was submitted, during coalification, to anisotropic stresses. If the stress was applied on a weakly thermally matured, still visco-elastic coal (microtexturally close to the 1B type), a 2B microtexture would be obtained. In contrast, if the stress was applied to brittle solids (microtexturally close to type 1A), a 2A microtexture was reached. The flattened pores could also result from the heat-treatment of 2B microtextured char.

The graphitization of the anthracites is similar to the graphitization of other microtextured chars, such as the chars obtained from the demineralization of lamellar silicate carbon nanocomposites : the ***in situ*** carbonization of polyaromatic molecules intercalated within the interlayer space of lamellar silicates leads to preferential planar orientations of type 2B and gives, at 2800°C, graphitized lamellar carbons [4].

To confirm our hypothesis, synthetic 2B and 2A microtextured chars should first be elaborated by applying anisotropic strains at different steps of the carbonization of thermally non graphitizable carbon organic precursors, and the structural and microtextural evolution, during a single thermal treatment at 2800°C, of such 2D microtextured chars should be compared to those observed for the anthracites.

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