A NOVEL MORPHOLOGY IN AN ANISOTROPIC PITCH ORIGINATED BY THERMAL TREATMENT

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Introduction

The evolution during carbonization and graphitization treatments of a 100% anisotropic pitch (pitch C) was compared to those of a classical isotropic petroleum pitch Ashland 240 (100% γ resins). The anisotropic pitch C results from a gas-sparge preparation leading to a composition of 93% β resins (QS-TI) and 7% γ resins (QS). It consists of a major anisotropic constituent having a poor preferred orientation inside which weakly anisotropic droplets specific to the gas-sparge process are dispersed [1,2]. The microtextural and structural evolution of the two pitches were studied by X-ray diffraction, optical microscopy (OM), transmission electron microscopy (TEM), and Vickers microhardness. In this paper, the peculiar behaviors during the carbonization and the graphitization of pitch C are reported [2,3].

Experimental

The heat treatment of pitch C and Ashland 240 was carried out in two steps. In the first one, the samples were heated to 1000°C at 4°C/min under an inert gas flow (PN_2 flow) and was then quickly cooled down. In the next step, the samples were heated in the range 1600°C - 2800°C under argon flow at an heating rate of 20°C/min and a 10min residence time at the selected temperature.

The samples were studied without extraction. For OM studies, they were embedded in an epoxy resin, polished, then examined between crossed polarizers with a λ plate added. Vickers microhardness measurements were performed on polished sections. To follow the progressive graphitization process X-ray diffraction (Siemens D500 powder diffractometer, Cu K (1 radiation) and TEM (Philips EM 400 and CM 20) were used. Degree of graphitization P_1, average interlayer spacing, and coherent domains size Lc and La were measured from the X-ray diffraction patterns. Thin sections of the ground samples were characterized by TEM using lattice fringes, dark field and electron diffraction modes. The TEM images were analyzed by image processing.

Results and discussion

The variation of Vickers microhardness versus HTT (Fig.1) shows that the both pitches are still plastic at 500°C. It is over 600°C that the material breaks without print, i.e. that solidification occurs.

Figure 2 shows OM images for pitch C and Ashland 240. Classical evolution is observed for Ashland 240. BT mesophase spheres develop in the isotropic pitch, then coalesce and 100% anisotropy is observed. The anisotropic domains of Ashland 240 are small and limited by disclinations. On the other hand, large and flat oriented

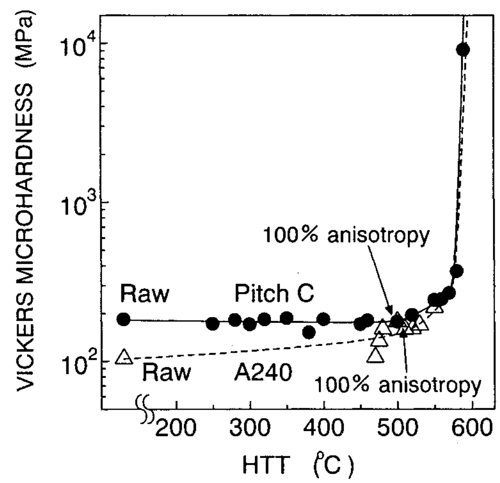

Figure 1. Vickers microhardness versus HTT for anisotropic pitch C (•) and Ashland 240 (Δ).

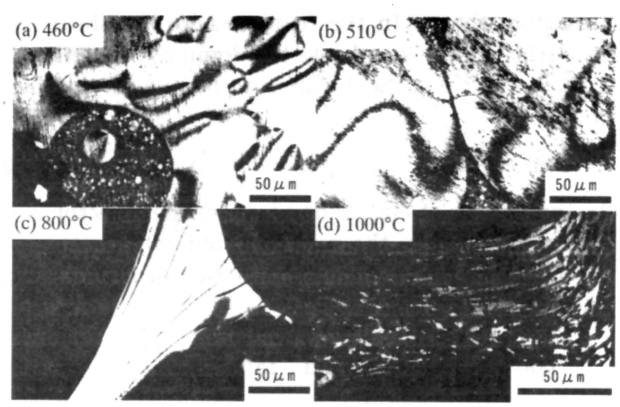

Figure 2. Optical microscopy images of pitch C and Ashland 240.

anisotropic domains are formed in pitch C.

The average interlayer spacing ($\overline{d}_{002}$), the coherent domains size Lc along c-axis, La (110) along a-axis and the degree of graphitization P_1 [4,5], which are obtained from the X-ray diffraction patterns, are given in Table 1. The data are close but the coherent domains size Lc and La is larger for heat treated pitch C while the best $\overline{d}_{002}$ values are obtained for A240 at high HTT.

For Ashland 240, the classical steps of graphitization occur. Between 1600 and 2000°C, columns disappears, lateral coherence leads to coalescence of adjacent BSU and continuous but distorted layers are formed. At 2000°C and above a complete annealing of the layer distorsions is observed and large polyedral pores with faces consisting of stiff layer stacks and limited by grain boundaries are formed.

For pitch C, during graphitization two kinds of morphology are found. The first one has the same thermal evolution as A240. The second one is peculiar and consists of an important stacking of carbon layers which lie perpendicular to the deposit plane of the particles (Fig.3). These particles are ribbon-like (Fig.4) with 500nm, or 2μm in width and 10μm in length and very thin since 002 lattice fringes are clearly observed at any place on the particle. From 1600 to 2800°C, as well as in 002 lattice fringes as in electron diffraction, the steps described for A240 are observed.

Conclusions

A novel morphology was underscored in TEM during graphitization treatment. It develops inside thin particles, micrometric in size, where carbon layers stacks lie perpendicular to the deposit plane. Thinking of separating them, a possibility arises to use them as a new precursor material for new applications.

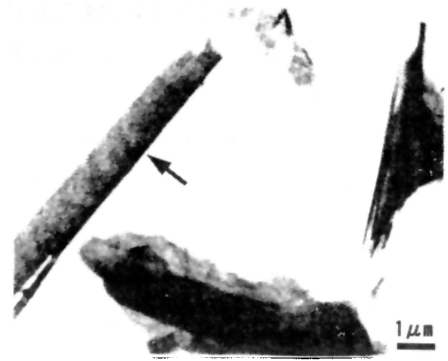

Figure. 3 TEM image of pitch C heat-treated at 2500°C. Specific morphology indicated by arrow is found among the normal phase particles.

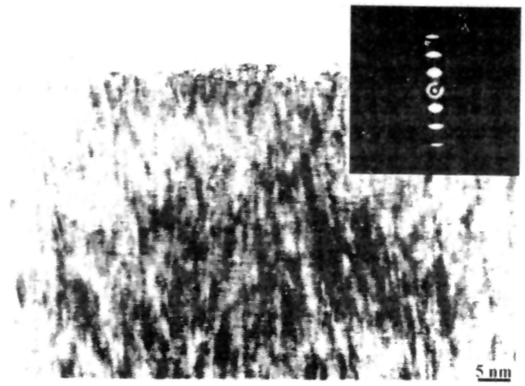

Figure.4 002 lattice fringe image, and selected area diffraction pattern of Pitch C heat-treated at 1900°C.

References

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Table 1. X-ray diffraction data for pitch C and Ashland 240.

Temperature	pitch C				Ashland 240			
	$\overline{d}_{002}$	Lc	La	P_1	$\overline{d}_{002}$	Lc	La	P_1
(℃)	(nm)	(nm)	(nm)		(nm)	(nm)	(nm)	
2000	0.3420	17.1	15.0	0.05	0.3430	10.3	17.5	0.20
2500	0.3378	28.7	35.0	0.46	—	—	—	—
2740	0.3380	32.5	32.5	0.50	0.3370	20.2	35.0	0.60
2800	0.3374	32.0	42.0	0.60	0.3360	28.6	37.0	0.63