THE STABILIZATION OF LARGE DIAMETER MESOPHASE PITCH FIBERS IN PURE OXYGEN AT LOW TEMPERATURE

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INTRODUCTION

Mesophase pitch-based carbon fiber has been recognized as an excellent filler for advanced composite materials[1]. The stabilization process, in which pitch fiber was oxidized to the thermosetting polymer to prohibit the adhesion and deformation of the filaments during the successive carbonization, is so slow that it is one of the most inefficient steps in the fiber production[2,3]. For the carbonized fiber thicker than 30 μ, the skin-core structure has been found to be introduced by the gradient of oxygen uptake in the radius of pitch fiber during the oxidative stabilization step [4,5]. The skin-core structure can be overcome by stabilization at lower temperature for longer time, since oxygen was permitted to have enough time to permeate into the center of thick fibers without excessive burn off on the surface. But thus, the step became very time-consuming and costly[4].

In the present study, the mesophase pitch fiber was stabilized in pure oxygen, not only to overcome the skin-core structure, but also to shorten the stabilization time by accelerating the rates of both the oxidization reaction and the diffusion of oxygen into the center of fibers.

EXPERIMENTAL

Petroleum derived mesophase pitch was spun into pitch fibers with the diameter of 40~ 45 μ. The stabilization of pitch fibers was carried out in pure oxygen at 240 ℃ for 10h in comparison with the case in air at 300 ℃ for 2h or at 240 ℃ for 20h at the heating rate of 2 ℃/min. The oxygen distribution in the cross-section of stabilized fibers was obtained with EMPA. The stabilized fibers were carbonized up to 1000 ℃ at 10℃/min. The tensile strength of carbonized fibers was tested. The transverse structures were observed under SEM(scanning electron microscopes).

RESULTS AND DISCUSSION

Fig.1 illustrates the oxygen distribution in the direction of radius for the stabilized fibers. Fig.2 shows the SEM photographs of the transverse structures of carbonized fibers. Tab.1 gives the conditions of oxidization and the strength of carbonized fibers.

For fibers stabilized in air at 300 ℃ for 2h, the gradient of the oxygen distribution along the diameter was very steep, the oxygen content at skin was 9.14%, but that in center was 0.83%(Fig.1a), its transverse section (Fig.2a) appeared distinctly skin-core structure with the area of core clearly indicating some fusion, and the tensile strength was low(Tab.1a). In the case of decreasing the temperature to 240 ℃ and increasing time to 20h, the oxygen gradient became flatter at the level of 7.22% to 4.16% (Fig.1b), the skin-core structure(Fig.2b) almost disappeared and the tensile strength was higher(Tab.1b). After stabilization in pure oxygen at 240 ℃, although the oxidation period was shortened from 20h to 10h, the oxygen distribution of the fiber was more homogeneous, ranging from 8.02% at skin to 5.24% in center(Fig.1c), no skin-core structure was observed(Fig.2c), and the tensile strength was the highest(Tab.1c).

On the basis of such observations, it can be noted how stabilization conditions determined the structure and properties of carbon fibers. Stabilization at high tempera -- ture was prone to introduce a skin-core structure in the carbon fibers because rapid

reaction at the surface prevented oxygen from diffusing into the center. Decreasing the temperature permitted oxygen to permeate slowly into the center. But it took a long time to reach the oxygen content necessary for the stabilization. Oxidization in pure oxygen overcame the skin-core structure as well as shortened the time. It can be assumed that oxygen partial pressure in the oxidative atmosphere and the stabilization temperature have different influences on the oxygen diffusion and the oxidation reaction. With increase of oxygen partial pressure, both reaction and diffusion can be accelerated. In contrast, the change of stabilization temperature mainly influences the rate of oxidization reaction.

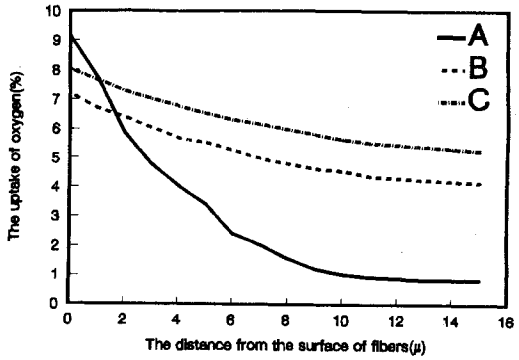

Fig.1 The distribution of oxygen uptake in the radius of oxidized fibers(The stabilization conditions are given in Tab.1).

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Tab. 1, The stabilization condition and the tensile strength of the carbon fibers

No.	atmos-phere	heating rate(℃ / min)	tempera -ture (℃)	holding time (h)	oxygen content (%)	tensile strength (MPa)	diameter of PF (μ)	diameter of μ CF μ (μ)
A	air	2	300	2	4.70	748	42	29.7
B	air	2	240	20	5.81	915	42	30.1
C	oxygen	2	240	10	6.64	917	42	30.8

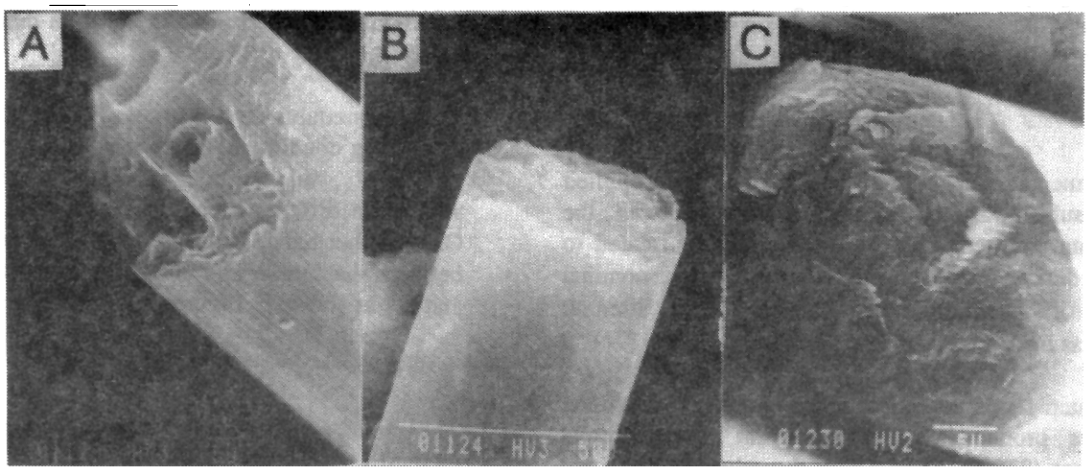

Fig.2, The SEM photographs of carbon fiber (The stabilization conditions are given in Tab.1).