DIMENSIONAL CHANGE OF ISOTROPIC PITCH-BASED FIBER DURING ACTIVATION

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INTRODUCTION

Activated carbon fibers have interesting properties since they can be arranged in diverse textile forms which gives a large flexibility in the design of filtration and adsorption devices. The small diameter of fiber minimizes diffusional effects and allows rapid adsorption and desorption rates of adsorbates [1]. Significant micropore volume can be introduced in these materials either by carbon dioxide or steam activation [2]. An important point in the activation process is to evaluate the amount of carbon which is gasified without formation of porosity, *i.e.*, the decrease in particle dimension by external gasification. In the present study isotropic-based carbon fibres were activated with carbon dioxide and steam in order to determine the fraction of external gasification to the development of microporosity.

EXPERIMENTAL

Ribbon-shaped fibres were prepared by melt spinning from an isotropic pitch (Aerocarb 80). The fibres were stabilized in air at 250 °C and carbonized at 900 °C. Mean length and width of fiber cross section are equal to 43 and 11 μm respectively. About 1 to 2 grams of fibres were gasified to different levels of burn-off at 900 °C under atmospheric pressure with pure CO_2 (linear gas flow rate equal to 36 cm/min) and steam diluted in argon (volumic ratio H_2O/Ar equal to 0.06 and gas flow rate equal to 125 cm/min) respectively.

Micropore volume of fibers was determined by physical adsorption of N_2 at -196 °C (micropores and supermicropores, V) and CO_2 at 0 °C (narrow micropores, V_{nar}) according to the Dubinin-Radushkevich equation in a way decribed elsewhere [3]. Carbon fibers were embedded in an unsaturated polyester resin and polished sections were observed in an optical microscope. Size and area of cross section was determined by an image analysis software and about 500-1000 fibers were considered for statistical meaning.

RESULTS AND DISCUSSION

The changes in V_{nar} and V of fibers as a function of burn-off for both types of activation are shown in Figure. 1. Narrow micropores are already present in the unactivated carbon fiber (V_{nar} = 0.19 cm^3/g). During activation, a substantial increase in V_{nar} is observed especially in the case of CO_2 activation. In fact at 40 % burn-off, V_{nar} is two times larger for CO_2 than for steam activation. The effect of gasifying agent is less pronounced on the development of micropore and supermicropore volume. As expected, V is somewhat larger for samples gasified in CO_2 than in steam. These results suggest that during activation with steam, enlargement of micropores takes place to a greater extent with steam than with carbon dioxide.

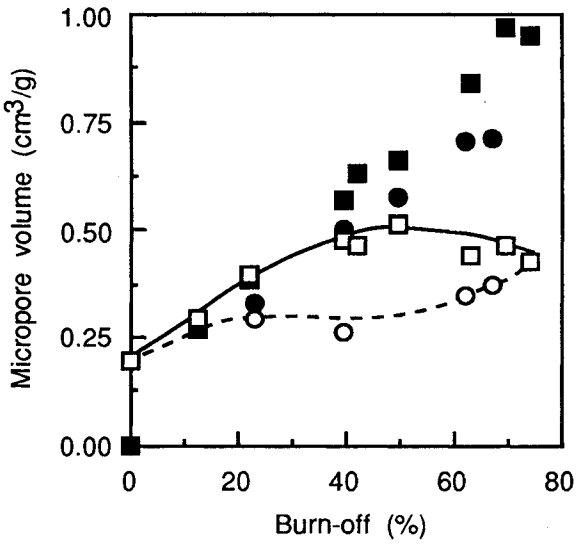

Fig.1. Micropore volume *vs* burn-off: (□), V_{nar} and (■), V for CO_2 activation; (O), V_{nar} and (●), V for steam activation.

Mean dimension of the cross section of the fibers decreases after gasification. The ratio of the length to the width remains nearly constant during activation which would indicate that the external part of the fiber is gasified at the same rate in both directions. The change of the mean cross section area of fibers, *a*, during activation is shown as a function of burn-off in Figure. 2. In the case of steam activation, *a* decreases gradually whereas with CO_2 a swelling of the cross section is observed between 40 and 50 % burn-off. The comparison of the histograms of the cross section area corresponding to fibers submitted

to 42 and 49 % burn-off indicates that the whole distribution is shifted towards higher values when the swelling effect is noticed. Hence an increase of the mean cross section is not due to an artefact like breakage of thinner fibers during sample preparation for image analysis and the swelling effect originates from a textural modification of the carbon fiber during activation in CO_2. Preliminary experiments carried-out with a circular pitch-based fiber gave similar results, *i.e.*, a swelling was observed only during activation with CO_2. Moreover, no significant change in fiber length was noticed during activation with steam or CO_2 below 60% burn-off.

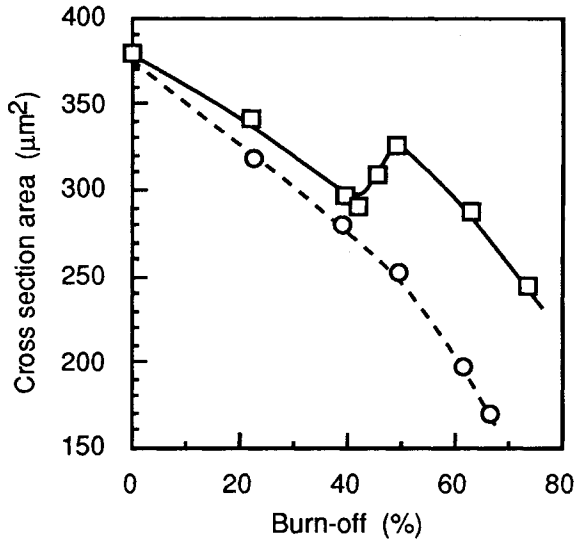

Fig. 2. Change in cross section area of fiber as a function of burn-off: (□), in CO_2; (O), in steam.

Pitch-based carbon fibers contain usually volatiles, mainly hydrocarbons and water. It was verified that fibers heat-treated at 900 °C for 30 hrs do not undergo any significant morphological change although their weight loss was equal to 15 %. Furthermore the heat-treated fibers still show the swelling effect during activation with CO_2. Hence a mere release of organic compouds during fiber activation cannot explain the increase in fiber cross section. Other heteroelements contained in these fibers are oxygen and, in a smaller amount, sulphur. The concentration of sulphur is equal to 1.7 % by weight for the untreated fibre and tends to increase after activation indicating that sulphur is only partially eliminated during gasification. The change in oxygen content with fiber burn-off is shown in Figure 3. Oxygen concentration basically decreases with burn-off by steam activation. In contrast, for fiber gasified in CO_2 a striking fluctuation in the content of oxygen is observed when the swelling effect takes place. An important amount of oxygen is found in the carbon once the swelling has started. Thereafter, it decreases again and its value becomes comparable to the one for fibers gasified in steam. These results suggest that during gasification in CO_2 an important network of narrow micropores is built-up mainly by opening closed pores when swelling is observed. Moreover the occurrence of a highly interconnected porous network may allow the fibre to 'swell' probably by stress relaxation. During activation by steam, the narrow micropore network is less developed and/or interconnected and no swelling is observed.

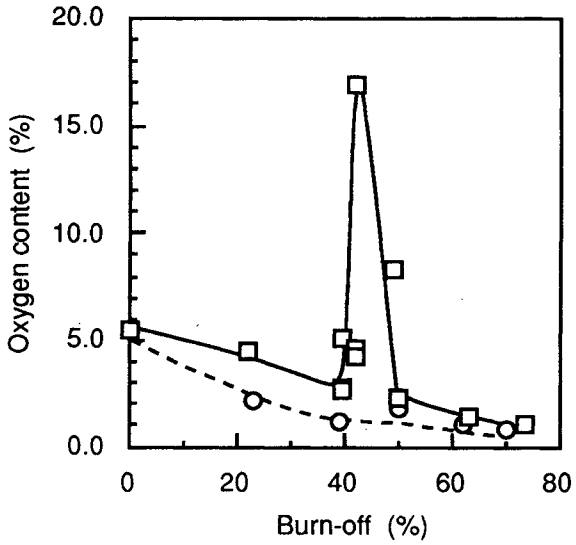

Fig. 3. Change in oxygen content of fiber as a function of burn-off: (□), in CO_2; (O), in steam.

CONCLUSION

The diameters of pitch-based carbon fibers decreases more during gasification in steam than with CO_2 indicating a more pronounced external burn-off. Moreover, during activation with carbon dioxide a swelling effect was found. This effect is due probably due to the development of an interconnected narrow microporosity expanding through the whole transverse direction of the fiber.

REFERENCES

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