EXFOLIATION OF CARBON FIBERS – EFFECTS OF HEAT-TREATMENT TEMPERATURE AND MICROTEXTURE IN CROSS-SECTION OF ORIGINAL CARBON FIBERS

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Intoroduction

The reports on exfoliation of carbon fibers through their intercalation compounds are very limited; ICl into pitch-based [1] and $SbCl_5$ into vapor-grown carbon fibers [2] in addition to the work on vapor-grown carbon fibers with potassium and tetrahydrofurane complex [3]. However nitric acid could successfully be intercalated into mesophase-pitch-based, PAN-based and vapor grown carbon fibers, by electrolysis and they could be exfoliated by rapid heating to 1000 °C by author's group[4].

Detailed studies on heat-treatment temperature (HTT) and cross-sectional morphology of original carbon fiber in various carbon fibers are required to develop new applications of these materials. In the present work, potential behavior with electrolysis in nitric acid and affect of cross section morphology in exfoliation were discussed in these carbon fibers.

Experimental

Mesophase-pitch-based carbon fibers heat-treated from 1150 to 3000 °C and having various cross-section morphology, flat layer, random and corrugate radial, are selected and listed in Table 1 together with sample code used in the present work. In those mesophase-pitch-based carbon fibers used, sizing agent was eliminated by heating them at 700 °C for 3 h in a flow of N_2, in advance to intercalation reaction. Intercalation reaction was carried out by electrolysis; on anode electrode of carbon fibers fixed to platinum plate by PTFE sealing tape were immersed into concentrated nitric acid electrolyte (13 N) and then applied 0.01 A to 1.0 A by using the potentiostat/galvanostat. The potential behavior with electrolysis at applied current in nitric acid for their carbon fibers were observed the dependence of passage time of electrolysis.

After electrolysis, carbon fibers were rinsed with water and then dried at room temperature in air. The intercalation compounds of the carbon fibers thus electrolyzed were rapidly heated in a tubular furnace kept at 1000 °C for ~3 second to be exfoliated. Carbon fibers were studied with X-ray diffraction (XRD) to measure the interlayer spacing by refering to inner standard of silicon and their morphology was observed under scanning electron microscope (SEM) with acceleration voltage of 5 kV.

Results and discussion

When the electrolysis of the carbon fibers was carried out with a constant current of 0.5 A in concentrated nitric acid solution (13 N), potential change of carbon fibers during their electrolysis markedly increased in two steps for mesophase-pitch-based carbon fibers heat-treated above 2000 °C (Fig. 1). On 1500 °C treated carbon fibers, MP-8, however, potential increased gradually, and almost no increase on 1150 °C treated ones. No difference of cross-sectional microtexture, random (MP-12), flat layer (MP-13) and corrugated radial (MP-14), could be recognized for potential change of its carbon fibers during their electrolysis (Fig. 2).

Fig. 3 shows comparison of XRD profiles of original carbon fibers, MP-7 to MP-11, and after the electrolysis and then drying in air. These carbon fibers heat-treated above 1500 °C give additional peaks near 2 = 11°, of which interlayer spacing are about 0.78 nm. The appearance of additional peaks proves the formation of intercalation compound of nitric acid

with stage-2 structure, which has been reported to have identity period Ic of 0.779 nm [5]. Therefore, 002 peak observed on the MP-8 to MP-11samples were supposed to be caused from residue compounds formed from intercalation compounds during rinsing with water and drying in air. On all carbon fibers heat-treated from 1500 to 3000 ℃, MP-8 to MP-11, and having various cross-section morphology, MP-12 to MP-14, exactly the same results were obtained, i.e., the formation of intercalation and residue compounds only in the anode electrode, which is reasonable with intercalation of acceptor NO_3^-.

These intercalation compounds exfoliated by rapid heating up to 1000 ^oC. After rapid heating to 1000 ℃, a marked morphological change was observed, a single fiber being converted to a bundle of thin filaments splitted along the original fiber axis. In the case of HTT was not determining factor for exfoliation; even 1500 ^oC treated ones could be exfoliated.

On other carbon fibers, MP-12, -13 and -14, the same exfoliation phenomena were observed by using SEM micrograph. No marked difference in morphology after exfoliation was detected between random and corrugate radial. However the exfoliation degree of flat layer seems to be larger than random and corrugate radial. On some fibers, the breaking of thin filaments perpendicular to the fiber axis was observed. The reason for this lateral breaking of filaments was not understood yet. It might be due to the cracks in the original fibers during manipulation.

Potential behavior to prepare the intercalation compounds and its exfoliation behavior of carbon fibers depended on crystallinity of original fibers (degree of graphitizationand) also on texture of fibers, particularly texture in their croos-section.

The exfoliated carbon fibers may create new applications and may be competitive with carbon nanofilaments (nanofibers) which recently attracted attention in various applications.

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References

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Table 1 Carbon fibers used.

Sample code	Precursor	Heat treatment temperature / ℃	Cross section
MP-7	mesophase-pitch	1150	Random
MP-8	mesophase-pitch	1500	Random
MP-9	mesophase-pitch	2000	Random
MP-10	mesophase-pitch	2500	Random
MP-11	mesophase-pitch	3000	Random
MP-12	mesophase-pitch	3000	Random
MP-13	mesophase-pitch	3000	Flat-layer
MP-14	mesophase-pitch	3000	Corrugate radial

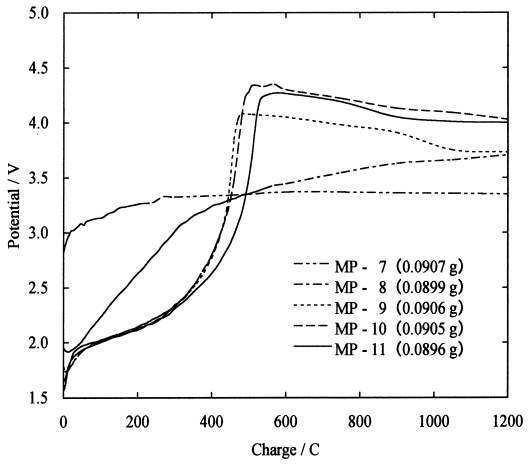

Fig. 1 Changes in the potential for mesophase-pitch-based carbon fibers through electrolysis at 0.5A for 50 min.

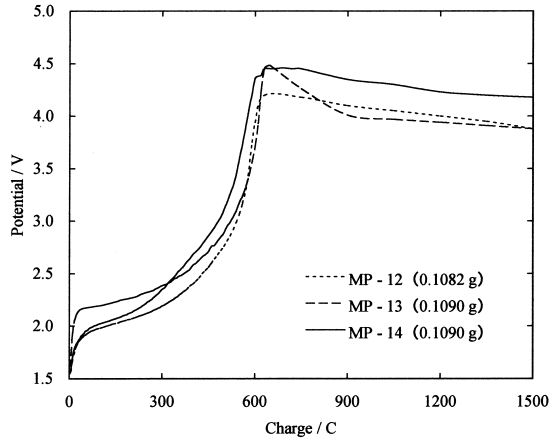

Fig. 2 Changes in the potential for mesophase-pitch-based carbon fibers through electrolysis at 0.5A for 40 min.

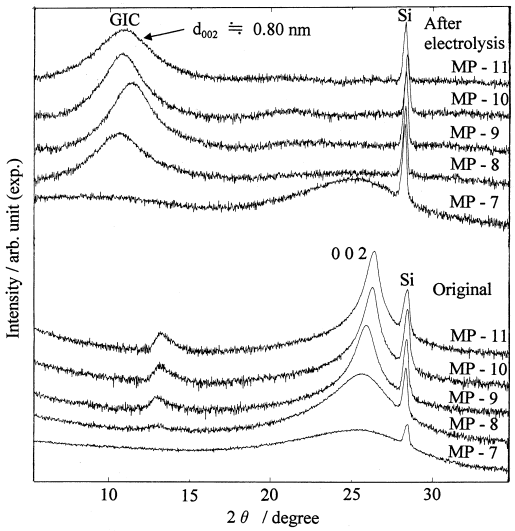

Fig. 3 XRD pattern of original and after electrolysis of carbon fibers.