# SURFACE TEXTURE WITH GRAPHITE STRUCTURE OF NON-GRAPHITIZING CARBON FIBER

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## Introduction

It has been known that carbon layers with graphite structure are formed on the surfaces of non-graphitizing carbons obtained from furan resin and cellulose with the shape of block or firm by heat treatment at high temperatures [1,2]. In the case of carbon fibers prepared from furan resin and cellulose, they are graphitized by stretching them during heat treatment at high temperatures [3]. However, the fibers heat-treated at high temperatures without stretching are not graphitized [3,4] and the texture and structure of the surfaces on the non-graphitizing carbons fibers have not been investigated. In the present study, the texture and structure of the non-graphitizing carbon fibers were examined, especially by focusing on their surfaces.

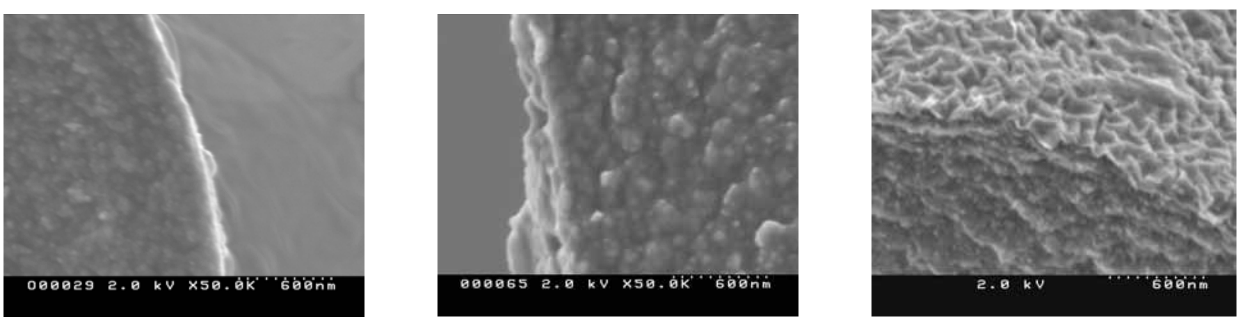
## Experimental

Two types of commercially available cellulose fibers were used. One is Lyocell with 1.5 - 3μm in diameter made from eucalyptus pulp by solvent spinning method. Another is Modal with 1.5 - 3μm in diameter made from beech pulp by viscose method. These fibers were produced by Lenzing Co., Australia and supplied by Moririn Co. Ltd. A commercially available phenol resin-based fiber Kynol KF0370 with 18μm in diameter was also used. The fiber was produced by Gunei Chemical Industry Co, LTD. These fibers were heat-treated to 900$^{o}$C with a heating rate of 2$^{o}$C/min in nitrogen atmosphere using an infrared image furnace and kept at this temperature for 2hrs. The 900$^{o}$C-treated fibers were further heat-treated to each desired temperature between 2400 and 3200 $^{o}$C with a heating rate of 20$^{o}$C/min in argon atmosphere using a graphite resistance furnace and kept at this temperature for 30 min. Another 3000$^{o}$C-treatment was made by the same method, but the graphite resistance furnace was broken when the temperature reached at 3000$^{o}$C. The samples thus heat-treated are denoted hereafter as 3000$^{o}$C-2. SEM observations were carried out for the surfaces and cross sections of these heat-treated carbon fibers. 002 X-ray diffraction measurements were made for the bundle of the carbon fibers using CuK$\alpha$ radiation and a specially designed holder.

Maximum transverse magnetoresistance $\Delta\rho/\rho$ was measured for each single filament of the carbon fibers at 77K in fields up to 1T. In order to examine the surface structure of carbon fibers, first order Raman spectra were measured for each single filament at room temperature in air using a 514.5nm line of an argon ion laser.

**Results and Discussion**

As examples, SEM images of cross sections of the phenol-based fiber Kynol KF0370 heat-treated at temperatures of 2400, 3000-2 and 3200 $^{o}$C are shown in Fig. 1. HTT in the figure captions means heat treatment temperature. A granular texture being characteristic of grass like carbon was observed on the cross sections for these carbon fibers. For the fibers heat-treated at temperatures above 2600$^{o}$C, as shown in Fig. 1 (b) and (c), different texture was found on the outer surfaces. The granular texture was also observed on the cross sections for the cellulose based carbon fibers. The different texture appeared on the surface of the fibers prepared at temperatures above 2400$^{o}$C, and the texture looks layered texture.




(a) HTT2400$^{o}$C (b) HTT3000$^{o}$C-2 (c) HTT3200$^{o}$C

Fig.1 SEM images of cross sections of phenol-based carbon fiber fibers.

Figure.2 shows the X-ray diffraction patterns for the phenol based carbon fibers heat-treated at temperatures between 2400 and 3000$^{o}$C as examples. Asymmetrical 002 diffraction patterns are observed for the carbon fibers at temperatures above 2600$^{o}$C and very similar to the patterns for cellulose carbon firms [1]. The results suggest that two components with different interlayer spacings exist in these samples. Suppose that each 002 pattern consists of only one component, the interlayer spacing $d_{002}$ for the carbon fibers is roughly evaluated to be 0.339~0.341nm after correction for Lorentz polarization and atomic scattering factors. The $d_{002}$ value indicates that these carbon fibers have turbostratic structure as a whole. The diffraction patterns for the cellulose based carbon fibers prepared at temperatures above 2600$^{o}$C are also asymmetry, and the fibers are regarded as turbostratic from their $d_{002}$ values obtained by the same way as that for the phenol based carbon fibers.

Figure.3 shows the field dependence of maximum transverse magnetoresistance $\Delta\rho/\rho$ at 77K for the phenol based carbon fibers as examples. All the specimen exhibit negative magnetoresistance. The negative magnetoresistance is characteristic of turbostratic structure. At a constant magnetic field, the absolute value of $\Delta\rho/\rho$ increases from HTT of 2400 to 2600°C, and then decreases. The absolute value increases with the progress of the turbostratic structure, but it decreases in the changing process from tubostratic structure to graphite structure or coexistence of both components [5]. $\Delta\rho/\rho$ is also negative for all the cellulose based carbon fibers heat-treated, and the similar change of $\Delta\rho/\rho$ by HTT was observed.

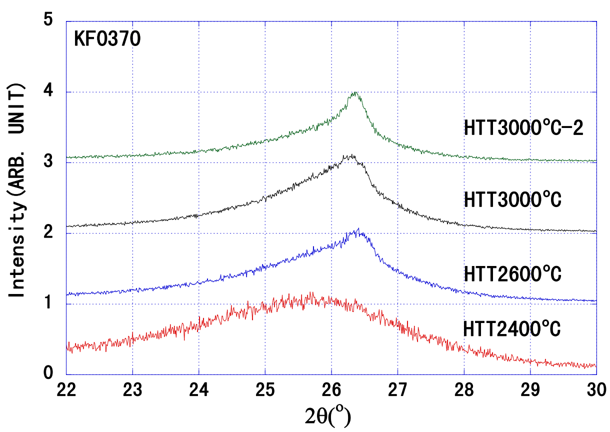



Fig. 2. X-ray diffraction patterns for phenol-based carbon fibers.

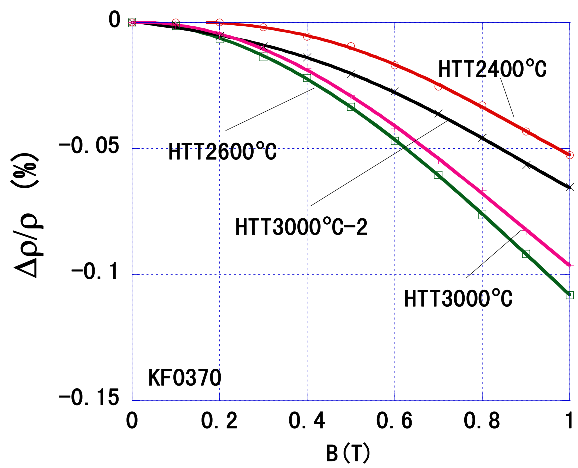



Fig. 3. Field dependence of maximum transverse magnetoresistance at 77K for phenol-based carbon fibers.

The first-order Raman spectra for the phenol based carbon fibers are shown in Fig. 4 as examples. The ratio of the D band to G band, $I_D/I_G$, in each spectrum is indicated in Fig. 4. The $I_D/I_G$ values for the fibers heat-treated at temperatures above 2600°C are below enough 0.2. The value obtained for vapor-grown carbon fibers (VGCF) heat-treated at 2600°C is about 0.2 [6]. VGCF is known to be high graphitizability, i.e. it graphitizes at HTT's above 2200°C and exhibits a marked development of graphitic structure with heat treatment [4]. The small $I_D/I_G$ values for the present phenol based carbon fibers, therefore, reveal that the surfaces of these fibers heat-treated at temperatures above 2600°C have graphite structure. The $I_D/I_G$ values obtained for the cellulose based carbon fibers prepared at temperatures above 2600°C are also below enough 0.2 and the surface layers on the fibers are regarded as graphite structure.

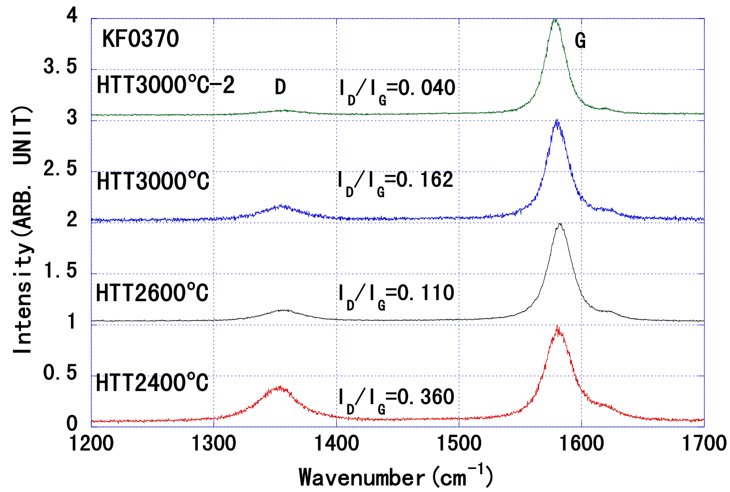



Figure. 4 First-order Raman spectra for phenol-based carbon fibers.

## Conclusion

Non-graphitizing carbon fibers with granular texture were prepared from commercially available furan resin and cellulose-based fibers. A different texture was formed on the surfaces of the carbon fibers by heat treatment at temperatures above 2600$^o$C. It was revealed that the different texture was composed of carbon layers with graphite structure.

## References

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