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Microstructure of Carbon Coils

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The as-grown carbon coils with three-dimensional/spiral morphology and amorphous structure grown via the decomposition of an acetylene gaseous at 700 to 900℃ were pre-treated to observe the microstructural change of the carbon coils, by heating at 1000 to 3000℃, the air and steam oxidations, the oxidation using nitric and sulfuric acids, the irradiation of ultrasonic wave to the carbon coils during the growth process. The heat-treatment leads to the developing crystallization of the carbon coils and the formation of capsule-like closed carbon layers of 10 to 20 layers with an inclination of 10 to 40° versus the fiber axis formed a "herringbone" structure in the edges of the carbon coils. The layer space (d) of the crystallized carbon layers was determined to be 0.341 nm, which is slightly greater than the calculated value of d=0.336 nm (JCPDS, No.23-64) and indicative of turbostratic structure. The oxidation of crystallized carbon coils brought the capsule-like closed layers of carbon coils into the partially opened layers.

Keywords: Carbon coils, microstructure, heat treatment, oxidation, crystallization

1. INTRODUCTION

In 1953, previous investigations have demonstrated that coil-like carbon can be fortuitously formed by pyrolyzing hydrocarbons in presence of CO under widely varying conditions.[1)] In 1990, carbon microcoils with a double helix structure (referred to as "carbon coils" hereafter) were repeatedly prepared by the catalytic pyrolysis of acetylene containing a small amount of sulfur or phosphorus impurity at 750-800°C[2-9)] and our research have simultaneously clarified the microstructure of carbon coils using TEM technique.[10,11)]

In this paper, the microstructures of carbon coils varied by each treatment: heating at 1000 to 3000°C, air oxidation under 5% air, were clarified using TEM technique.

2. EXPERIMENTAL

The as-grown carbon coils were pre-heated at 1000 to 3000°C for 1hr under Ar atmosphere to crystallize them. The pre-heated carbon coils were oxidized at 1000°C for 5 or 10min under the mixture gas of 5Vol%Air–95Vol%Ar. These pre-treated specimens were milled by ion-beam to transverse it by electron beam of TEM. The milled specimens set on the micro grid

mesh were observed to clarify the crystal structure by the TEM techniques: the dark and bright-field images, high-resolution image.

3. RESULTS AND DISCUSSION

3.1. The morphology of the as-grown carbon coils

The carbon coils whose tip have Ni compounds were formed by the catalytic pyrolyzing of acetylene mixture gas with sulfur and phosphorus at 750-800°C, as shown in Fig. 1. The cross-sections of fibrous carbon coils have the square and circular shape of Fig. 2. Figure 3 shows the elongation state of carbon coils; (a) no elongation, (b, c) weight was loaded on the carbon coil. The carbon coils with square shape always elongate keeping the double helix structure.

3.2. The crystal states of the carbon coils by heat-treatment

Figure 4 indicates the X-ray diffraction patterns of the as-grown carbon coils and the carbon coils heat treated at 2300, 3000°C under air atmosphere. The as-grown carbon coils have mostly amorphous structure. The diffraction peaks of carbon coils increased with the increase of heat treatment temperature. Especially, the 002 peak position of the carbon coils heat treated at 3000°C tended to shift to high diffraction angle of 2θ. This declination of peak position indicates the decrease in the d space between carbon layers.

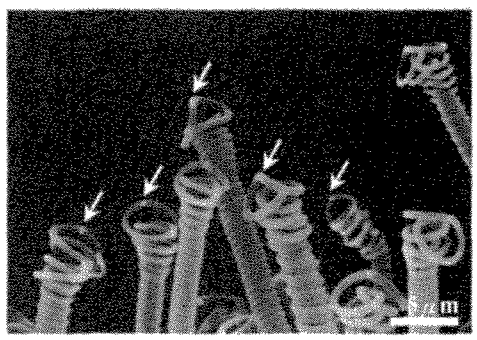

Fig. 1 SEM photograph of CMC (Arrow: Ni compound).

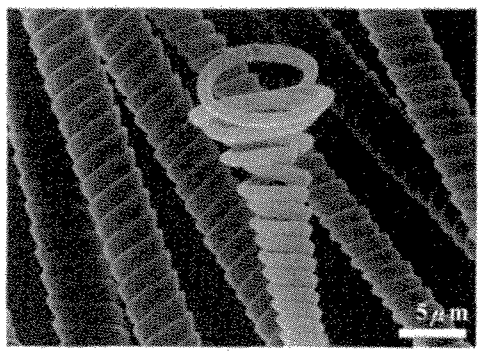

Fig. 2 SEM photograph of planular CMC.

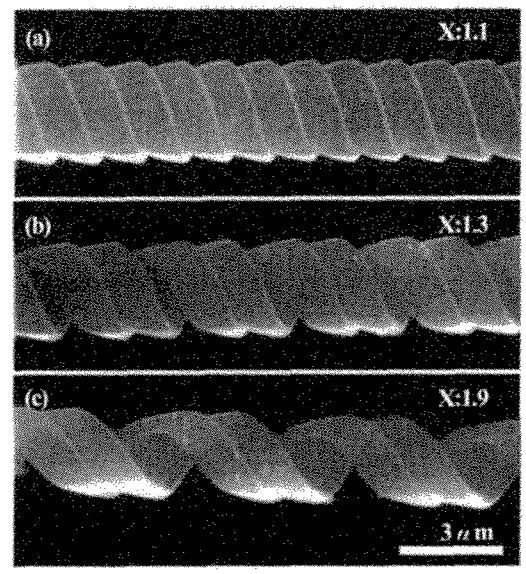

Fig. 3 The state of elongation of CMC. (a) No load, (b, c) Load.

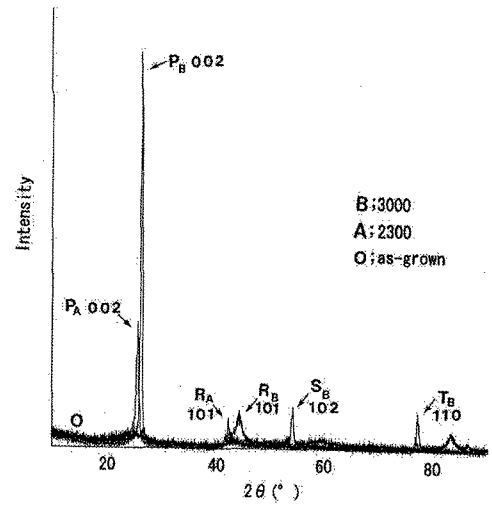

Fig. 4 X-ray diffraction patterns of CMC heat -treated in Ar. O: as grown, A: 2300°C, B: 3000°C.

The herringbone structure of carbon coils with the convexo-concave edges was obtained by milling the carbon coils, as shown in Fig.5. This fractural shape reflects the single crystal of Fe compound. The electron diffraction patterns of carbon coils indicate partially the alignment of carbon layer since the arc-like 002 diffraction rings were confirmed in Fig.5 (a).

The diffraction rings of the carbon coils heat treated at 1000°C indicate the clear orientation to 002. In the case of heating at 2300°C, the arc-like 110 and 101 lines appear and the spotty rings of 002 were also confirmed. The electron diffraction indicates the three spots of 002 at 2800°C. The crystallization of carbon coils would be accelerated by the heat treatment of more than 2300°C.

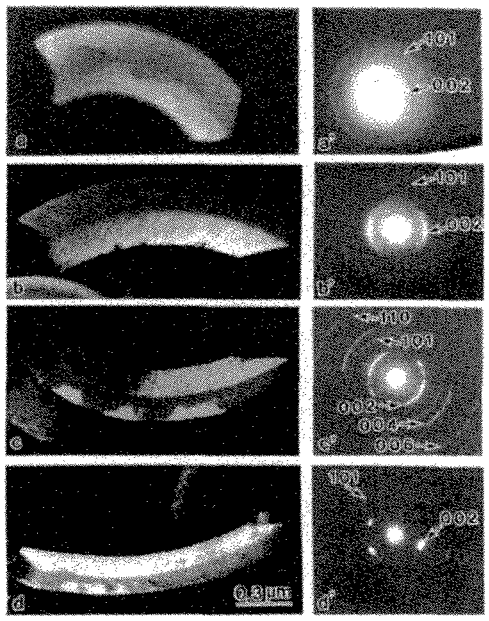

Fig. 5 TEM photographs of dark field and diffraction of fractional CMC heat-treated.
(a) as grown, (b) 1000°C, (c) 2300°C, (d) 2800°C.

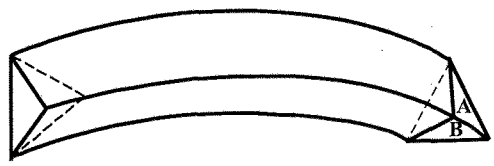

Fig. 6 Schematic image of the herringbone structure of the graphite coils with pyramidal graphite layers. A: Growth plane most activated by Ni_3C grain, B: Growth plane with small activation.

Schematic image of the herringbone structure of the crystallized carbon coils with the pyramidal convexo-concave edges is shown in Fig. 6. The different growth velocity between A and B planes seems to bring the curved shape of carbon filament.

The electron diffraction of area P at the tip of a fractural carbon filament in Fig.7 (a) is shown in Fig.7 (c). Figure 7 (b) indicates the high-resolution image of area P. The 0.341nm of d space between carbon layers is corresponding to that of the Vapor Growth Carbon Fibers (VGCFs) synthesized by Liquid Pulse Injection (LPI) technique[13]. The capsule-like carbon layers of 10-20 lines occur since the surface energy at the edge of carbon layers is unstable as shown in Fig. 7 (d).

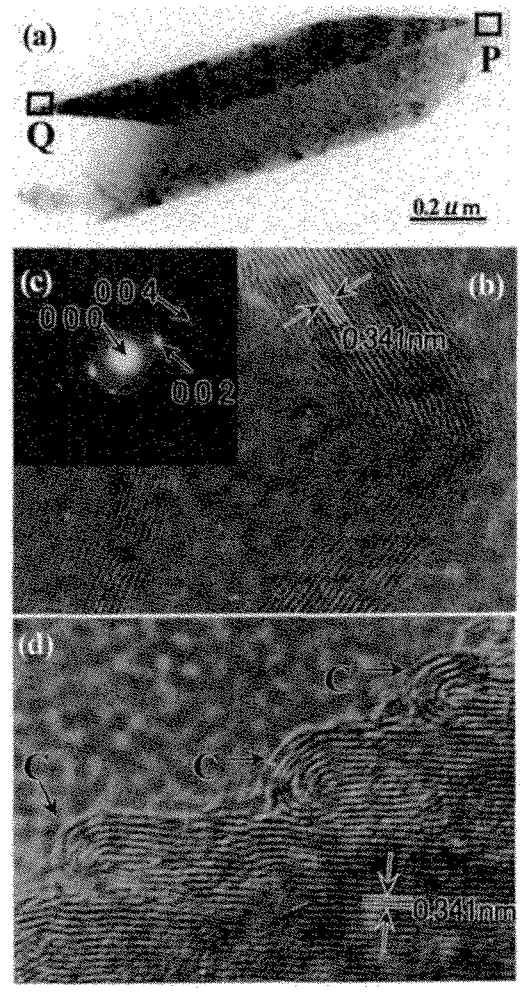

Fig. 7 High-resolution photographs of CMC heat-a treated at 3000°C.
(a) Whole view, (b) Macro photograph of P,
(c) Diffraction pattern of P,
(d) Macro photograph of Q,
(C) Completely closed cap.

3.3. Air oxidation of the carbon coils heat treated at 3000°C

The microstructure of the carbon coils heat treated at 3000°C

were not varied by the air oxidation at 1000°C for 5min in Fig.8-(a) and but the closed capsule-like carbon layers composed of 10-20 layers were also partially changed into the opened carbon layers by the oxidation at 1000°C for 10min in Fig.8-(b). Thus microstructural variation of the carbon coils indicates the possibility to control the electronic or the electromagnetic properties.

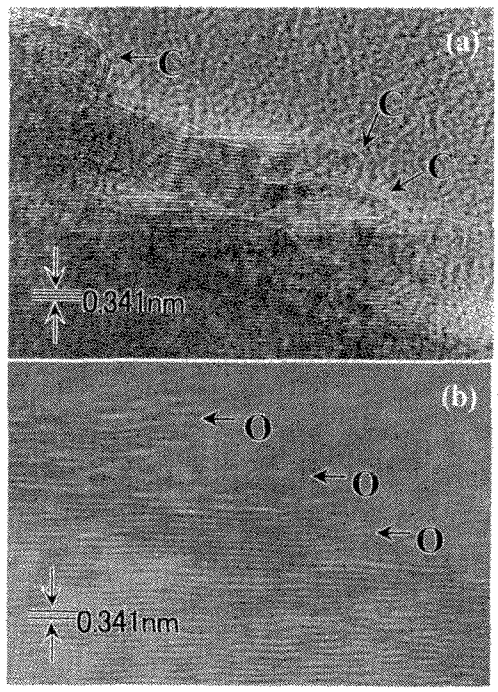

Fig. 8 The effect of oxidation of CMC heat-treated at 3000°C on the microstructure of graphite layer.
(a) 1000°C-5min in 5% air,
(b) 1000°C-10min in 5% air,
(C) Completely closed cap,
(O) Completely opened cap.

4. CONCLUSIONS

The microstructural change of carbon coils by the pre-treatment: heating at 1000 to 3000°C for 1hr under Ar atmosphere and oxidizing at 1000°C for 5 or 10min under the atmosphere of 5Vol%Air-95Vol%Ar, was investigated using TEM techniques. The structure of the as-grown CMC with amorphous structure was converted into the crystallized structure with considerably developed carbon layers by heat treatment. The capsule-like closed carbon layers were changed into the opened carbon layers by oxidation of the carbon coils.

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