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Morphologies, Microstructure and Growth Mechanism of Carbon Nanocoils over Stainless Steel Catalysts

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Chiral single-helix twisting carbon nanocoils with a fiber diameter of 50-500 nm, inner coil diameter of zero, coil gap of 0-100 nm, were prepared in large scale by pyrolysis of acetylene over the stainless steel catalysts under the presence of sulfur, the morphology and microstructure were examined. The catalyst grains on the growth tip of nanocoils were observed closely.
Keywords: Carbon nanocoil, Stainless, Microsructure; Morphology; CVD

1. INTRODUCTION

Carbon nanomaterials such as carbon nanotubes [1-4], carbon nanofibers [5-6], are now at the forefront of nano-materials science because those materials have many potential applications such as nanoelectronic devices, hydrogen absorption materials, etc. The relating research work play an important role in understanding some fundamental concepts, for example, the effects of dimensionality, morphology, chirality and microstructure of the nanomaterials on optical, electronic, electromagnetic, magnetic and mechanical properties.

On the other hand, the so-called catalytic decomposition of hydrocarbons or carbon monoxide disproportionation, which stand on the chemistry of solid–gas reactions on a metallic surface, are the only viable solutions offering less energy consumption and easy scaling up compared to other production methods, such as the electric arc discharge or laser ablation of graphite. By this method, various carbon materials with different structures and conformations can be obtained, especially by acetylene pyrolysis over Fe-alloy catalysis.

The carbon microcoil/nanocoil is one kind of vapor grown carbon fibers with specific regular 3D-helical/spiral conformations and amorphous structure. Although helical carbon nanofibers were occasionally observed by carbon filament researchers [7-13], mass production of the carbon microcoil/nanocoils have not been extensively reported by other researchers until S. Motojima et al. [14-28] found that the three-dimensional-curled carbon microcoils/nanocoils could be obtained by the catalytic pyrolysis of acetylene. We have reported the carbon microcoils prepared by Ni-catalyzed pyrolysis of acetylene. We also found that Fe was not a suitable catalyst for the growth of carbon microcoils [12]. However, recently, we developed a serious of Fe-containing alloy catalysts, and found that catalysts containing iron were good for the growth of twisting carbon nanocoils. In this study, morphology and microstructure of carbon nanocoils obtained by catalytic pyrolysis of acetylene using stainless steel (Fe-containing alloy) catalysts are reported.

2. EXPERIMENTAL

A vertical quartz tube (6×10^{-2}m, i. d.), which has an upper source gas inlet and a lower gas outlet, was used as the reaction tube. The Fe-group alloy powders were used as the catalysts and graphite plates as the substrate, which were set in the center of the reaction tube. The quartz reaction tube was heated by nichrome elements from the outside. The source gas mixture of C_2H_2, N_2, and a S-containing promoter were vertically introduced onto the substrate surface from the upper gas inlet, and purged from the lower gas outlet. The gas flow rate of C_2H_2, N_2 and the promoter was adjusted in 10-60 ml/min, 100-280 ml/min, and 1-20 ml/min, respectively. The reaction temperature was 650-800℃. The morphology of the deposits and the catalyst grains observed on the growth tip of the carbon nanocoils were examined closely by SEM and the microstructure of the carbon nanocoils was examined by TEM. The chemical compositions of the catalyst grain were detected by EPMA.

3. RESULTS AND DISCUSSION

It was found that when using a Fe dominant alloy (stainless steel) as the catalyst at the reaction temperature of 650~800℃, thick carbon fibers with a diameter of several hundreds micron were formed, and twisted carbon nanocoils were formed on the carbon fiber surfaces after a reaction time of about 5 mins.

Fig. 1 shows a typical cross section of a thick carbon fiber with a diameter of several hundreds micron and a length of several millimeter, on the thick carbon fiber the nanocoils begin to grow on the surface at the reaction time of 30 min. Fig. 2a gives a low magnification SEM image of the nanocoils, while Fig. 2b shows the typical enlarged view of the morphology of carbon nanocoils. Fig. 3 gives an enlarged view of the cross section morphology also exhibits the surface morphology. It can be seen that the carbon particles deposited in a ring-layer upon another ring-layer; the carbon particles size is less than 20 nm. The nanofibers of a diameter of 100~500 nm coiled in

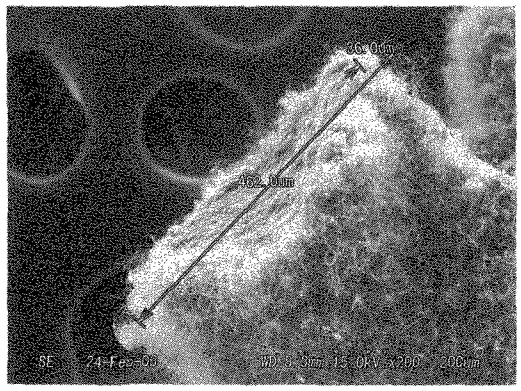

Fig. 1 Twisting carbon nanocoils grown on the surface of a thick carbon fiber.

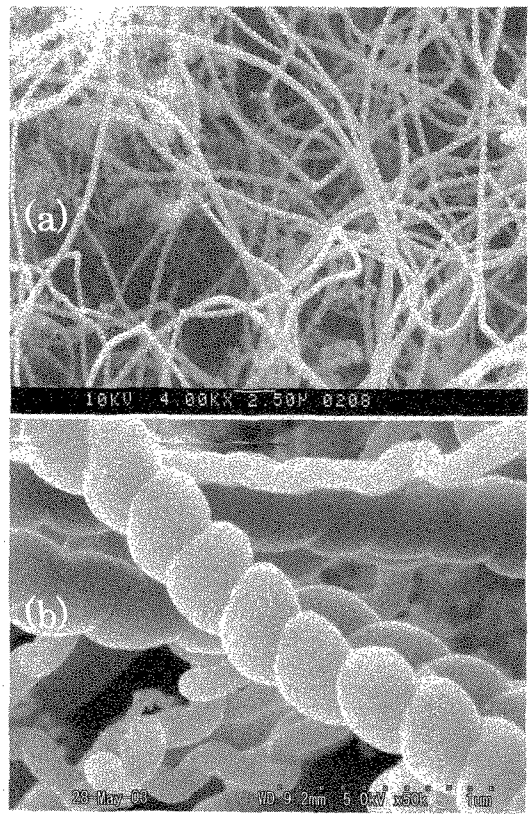

Fig. 2 Mass amount of twisting carbon nanocoils grown on the surface of thick carbon fibers.

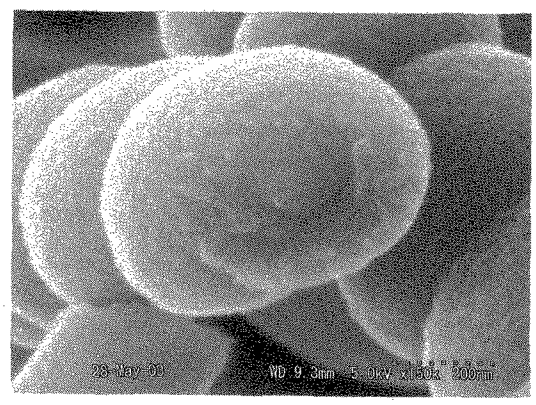

Fig. 3 Microstructure of the twisting carbon nanocoil.

twisting form, the inner coil diameter is zero, the out diameter is larger than the fiber diameter, the coil pitch is the same or slightly larger than the fiber diameter, and the coil length is about several hundred microns. Comparing with carbon microcoils which grow on the so called "hard carbon layer" [20] (It is actually a layer of carbon alloy formed in the induction period), suggesting that during the growth of carbon microcoils and nanocoils, the active catalyst composition is not metals, but metal-carbon alloy, but the alloy composition may be different.

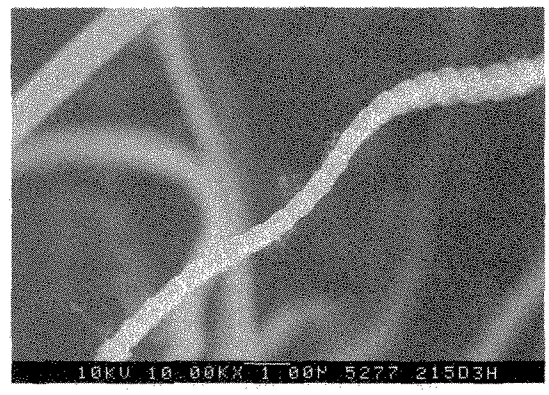

Fig. 4 Zigzag carbon nanofiber.

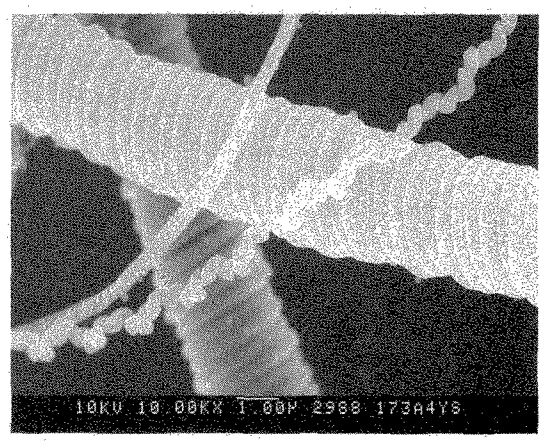

Fig. 5 The carbon microcoil co-grew with the twisting carbon nanocoil.

It is common that zigzag fibers were observed among the twisting carbon nanocoils. The morphology of the zigzag carbon nanofibers is also shown in Fig. 4. The zigzag nanofibers are composed of twin fibers, curling with a regularly continuous s-shape, 2-dimensionally and periodically. They are actually 2D-spiral carbon nanofibers with chirality alternating along a piece of a coil.

Fig. 5 presents an SEM image of a super-helix nanocoil (the twisting nanofiber spirals in a pitch of about 2 micron) which co-grew with carbon microcoils, this image gives a good morphology comparison between the two kinds of carbon coils. The carbon microcoils are actually double-helix coiled tube (or microsolenoid due to no coil gap) with coil diameter

of 4 microns, the secondary fibers are circular cross section as described in Ref. 18. The diameter of the nanofiber, which composed the twisting nanocoi,l is about 400-500 nm, while the fiber width of this microcoil is about the same. For comparing with carbon microcoils further, Fig. 6 shows a flat-fiber carbon microcoil with a fiber width of about 1 μm and a coil diameter of about 5 μm, the cross sections show that carbon deposited in rectangular layers, the two flat fibers coiled in a same left-hand coiling-chirality. A representative growth tip of carbon microcoils is shown in Fig. 7, the arrow indicates a crystal grain, from which two fibers grew, coiling in the same coiling chirality because of the catalyst anisotropy as proposed in Ref. 19.

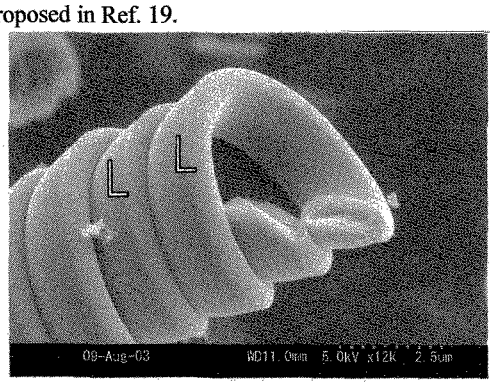

Fig. 6 Cross sections of a flat-fiber carbon microcoil.

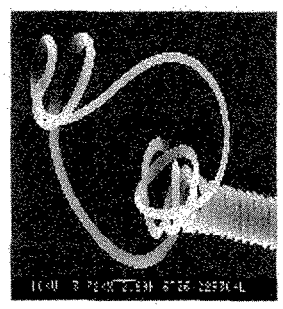

Fig. 7 A growth tip of a carbon microcoil.

While in this work, two nanofibers grew out of the catalyst grain twisted in different chirality (Fig. 8a), that is, two fibers are in mirror-symmetry, this is a two-directional growth mode. However, sometimes growth pattern of twisting nanocoils are not symmetry as shown in Fig. 8b. Furthermore some twisting nanocoils are grown by one-directional growth mode as shown in Fig. 9, this coil is a right-hand coil, and between the catalyst gain (the arrow) and the coiled part, there is a straight part. C, Fe, Ni, Cr, S and O were detected in this brightened part by EPMA. Electron diffraction results proved that the composition of the growth tip is Fe_2C_5 single crystal, in the monoclinic crystal phase; some of the Fe atoms were substituted by Ni, some by Cr.

It is very interesting to observe that along with one fiber, the twisting (coiling) direction of the coil changed from L to R (or R to L). It is also common to observe the alternation from twisting-form to straight-form, or aversely. That is, the coiling-chirality changes during the growth, Fig. 10 shows the example. In Fig. 10, we can suppose that in the position where the chirality changed, there may be catalyst grain, but no such evidence has been obtained, However, it may be considered that the coiling-chirality change of nanocoils is the result of releasing fiber stress which is caused the small coil diameters.

The microstructure was observed by TEM, given in Fig. 11, (a) is before heat-treatment, (b) is after heat-treatment at 2500 ℃, for 30 min in N_2 atmosphere. Before the heat-treatment, the TEM image indicates that it is a herring-bone structure, after the heat-treatment, the much clearer herring-bone structure was observed.

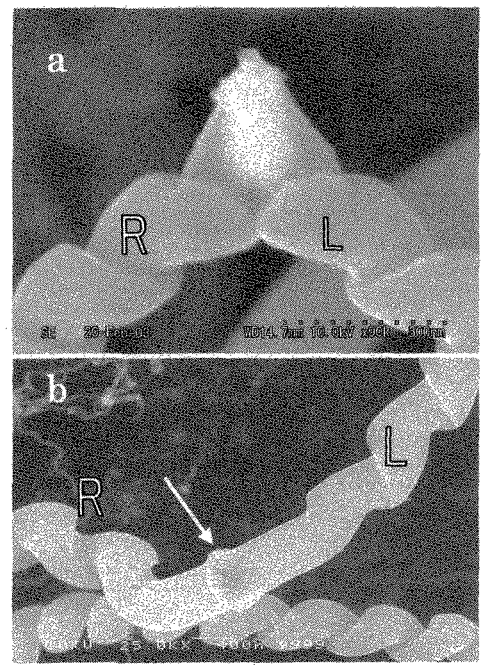

Fig. 8 Growth tips of the twisting carbon nanocoils.

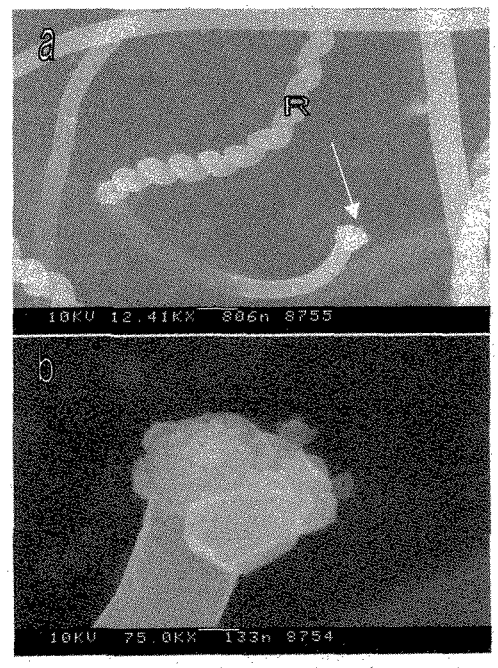

Fig. 9 Another growth tip of the twisting carbon nanocoil which is of one-directional growth.

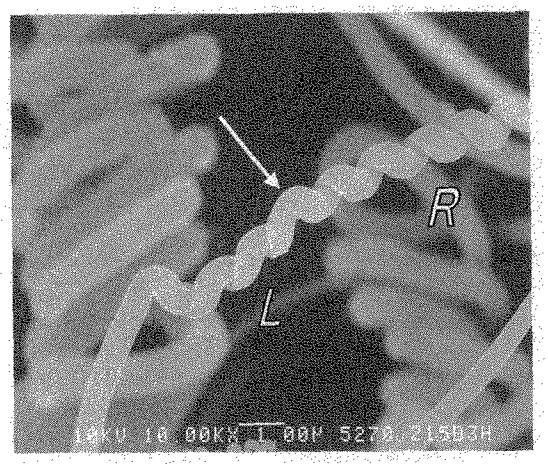

Fig. 10 Twisting carbon nanocoil with coiling chirality changed.

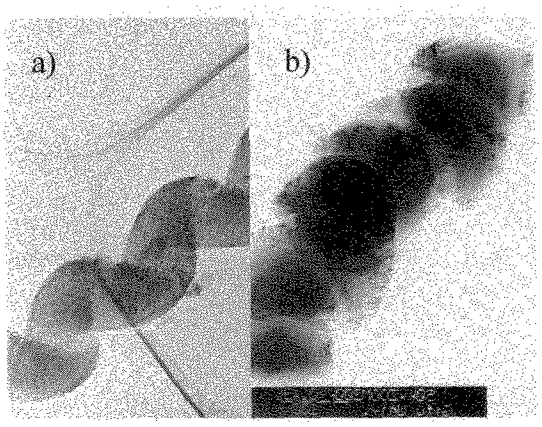

Fig. 11 Herring-bone structure of the carbon nanocoil shown by TEM. a): before Heat-treatment, b): after heat-treatment.

4. CONCLUSIONS

Chiral single-helix twisting carbon nanocoils with the fiber diameter of 50-500 nm, inner coil diameter of 0 nm, coil gap of 0-100 nm, were prepared by pyrolysis of acetylene over the stainless steel catalysts under the presence of sulfur, the morphology and microstructure were examined. The catalyst grains on the growth tip of nanocoils were observed closely, which indicated that two twisting nanocoils grew out of a catalyst grain in opposite chirality. The fibers are grown in the herring-bone structure. It is very interesting to observe that along with one fiber, the twisting (coiling) direction of the coil changed from L to R (or R to L). It is also common to observed alternating from twisting-form to straight-form, or aversely. That is, the coiling-chirality changes during the growth.

Acknowledgement

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