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Preparation of Carbon Microcoils/Nanocoils and their Morphologies

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Carbon microcoils/nanocoils (CMC/CNC) with a 3D-helical/spiral structure, and with the coil diameter size of micron to nanometer order were prepared by the catalytic pyrolysis of acetylene using Ni, NiS, Mo, Cr, stainless steel, and WS_2 catalysts. The morphologies of the grown CMC/CNC were examined in detail. Using a Ni powder, the regular coils with a constant coil diameter through a piece of coil and irregular coils with different coil diameters and pitches as well as straight carbon fibers were generally simultaneously obtained. The obtained coils were generally double-helix coils. Using the most regulated conditions, the regular coils were obtained with high coil yield. While using fine Ni catalyst, some amount of the single-helix CNCs was obtained. Using stainless steel catalysts, a large amount of the single-helix CNC with a twisted-form were obtained. Furthermore, using WS_2 catalyst, multiple-helix CNC or single-helix CNC with dumbbell-type fiber cross-section as well as regular single-helix CNC could be obtained. These morphological changes may be caused by the different shapes and catalytic activities of the catalyst grain.

Key words: carbon nanocoil, vapor grown carbon fiber, acetylene, catalyst, CVD

1. INTRODUCTION

Recently, the growth of helical-coiled carbon nanotubes or nanofibers was sometimes observed during the preparation process of carbon nanotubes or nanofibers by the catalytic pyrolysis of hydrocarbons [1-3]. These coiled nanotubes or naofibers have the coil diameter of several tens to several hundreds nanometers and the coil pitch of several tens nanometers to several tens micrometers while the diameters of the fibers, by which coils are formed, are smaller than 100 nm. We refer the helical-coiled carbon tubes or fibers with coil diameters less than submicron size (several hundred nanometers) as "carbon nanocoils (CNC) " in contrast to the "carbon microcoils (CMC)" with a micron-order coil diameter. We have prepared very regular-coiled carbon microcoils (CMC) with a good reproducibility and a high coil yield by the catalytic pyrolysis of acetylene containing a small amount of sulfur or phosphorous impurity [4-6]. We also prepared the carbon nanocoils [CNC] using fine Ni powder or sputtered metal thin films as the catalysts [7]. These carbon coils are expected to have many novel and critical functionalities due to their characteristic 3D-coiling morphology. Accordingly, these carbon coils are very interesting as a high potential candidate for many applications, such as electromagnetic wave absorbers, tunable micro-devices (microsensors, microactuators, micro- machines, etc.), field electron emitters, chiral catalysts, etc.

In this study, we obtained carbon microcoisl/nanocoils (CMC/CNC) with the coil diameter of several hundred micrometer to nanometers and the coil length of 1-3 mm using a metal powder catalysts under applying a magnetic field to the reaction zone, or using sputtered thin films of metals or alloys as the catalyst at 600-800°C. The morphologies of the obtained CMC/CNC using various catalyst were examined in details.

2. EXPERIMENTAL

The preparation of the CMC/CNC was carried out by the following thermal CVD device. A horizontal quartz tube (30 mm i.d., 700 mm length), on the central part of which a vertical gas inlet and outlet are attached, was used as the reaction tube. As a catalyst, powder or sputter-coated thin films of Ni, Au, etc. were used. The sputter-coated films were obtained on a substrate by an ion coater. The graphite plate was usually used as the substrate. The source gas mixture of C_2H_2, N_2, and H_2S 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 H_2S was 10-80 ml/min, 50-300 ml/min, and 0.1-10 ml/min, respectively. The reaction temperature was 600-800°C. The obtained carbon deposits were observed by FE-SEM.

3. RESULTS AND DISCUSSION

3.1 By Ni and NiS catalyst

As a carbon source, acetylene was the most useful for the growth of the CMC/CNC. The small amount of sulfur impurity was indispensable for the growth of carbon coils. For obtained CMC, fine Ni powder was the most effective catalyst among the pure metal catalysts used, while stainless steel was the most effective catalyst among the alloys or compounds used. It was found that the coil diameter could be reduced by applying magnetic field in the growth atmosphere and zone of the CMC to form the CNC from the outside of the

reaction tube using a permanent Nd-Fe-B magnet of max. 1T. Fig. 1 shows the CMC with various morphologies obtained using Ni powder as the catalyst (average grain size: about 5 μm) at 770℃. The regular carbon coils (Fig. 1a) have a constant coil diameter of 3-5 μm though the coil length. The optimum reaction conditions for obtaining these regular coils with high coil yield was as follows; temperature 750℃, gas flow rates of C_2H_2, N_2 and H_2S was 60 ml/min, 200 ml/min, and 0.1~20 ml/min, respectively. Deviation from these optimum conditions resulted in the formation of the irregular coils of irregular coil diameter and coil pitch, as shown in Figs. 1b and 1c. Using a Ni catalyst, the CMC with various interesting morphologies such as shown in Figs. 2 and 3 were observed. Fig. 2 shows the twined double-helix coils composed of different coil pitch and thus different coil length. Fig. 3 shows the double coils composed of two fibers with different rectangular fiber cross-section, in which long axis of two fibers were perpendicular each other.

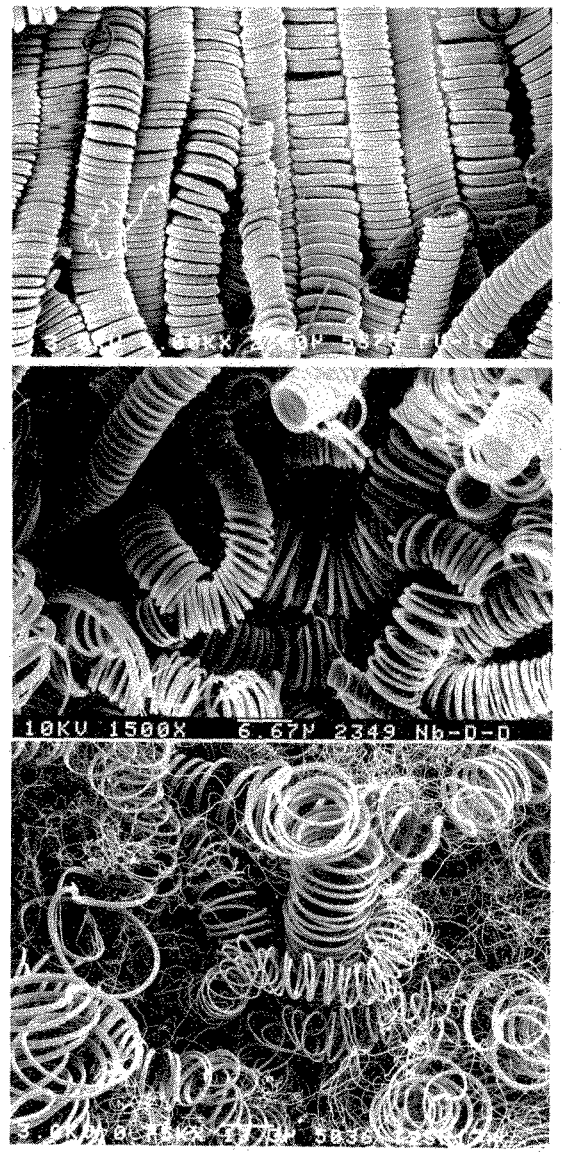

Fig. 1. Carbon microcoils with different coiling morphologies.

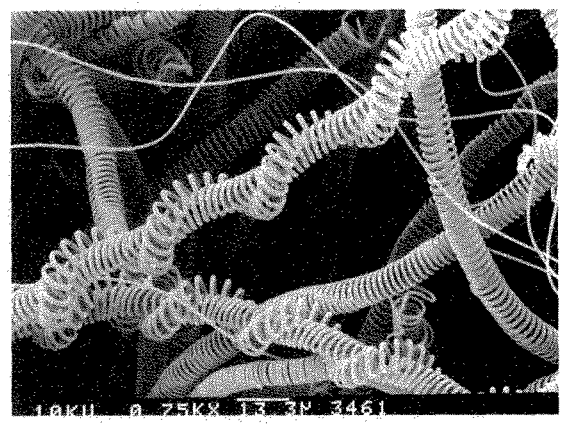

Fig. 2. Twined carbon microcoils.

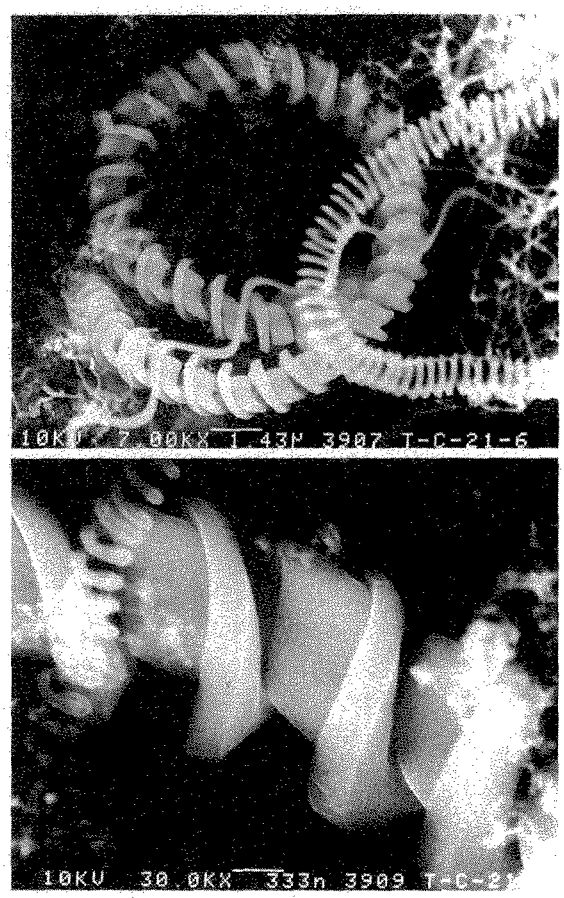

Fig. 3. Double-helix carbon microcoils composed of two fibers with different fiber cross sections.

Using fine Ni powder (about 50 nm diam.) catalyst, small amount of CNC were obtained. On the other hand, under a concerted reaction field with applying hybrid energetic field , the fibers coiled with much smaller coil diameter to form the CNC with several hundred coil diameters. Fig. 4 shows the CNC obtained using fine Ni powder catalyst under the concerted reaction atmosphere. It can be seen that a lot of the CNC with an outer coil diameter of about 500 nm were grown among the CMC with an outer coil diameter of about 5 μm and noodle-like carbon twin-fibers with the fiber width in the

same order. It was observed that these CNC have generally single-helix twisted form with zero inner coil diameter, while the spring-like form double-helix CMC have several μm inner coil diameter, as can be seen in the enlarged view (Fig. 5).

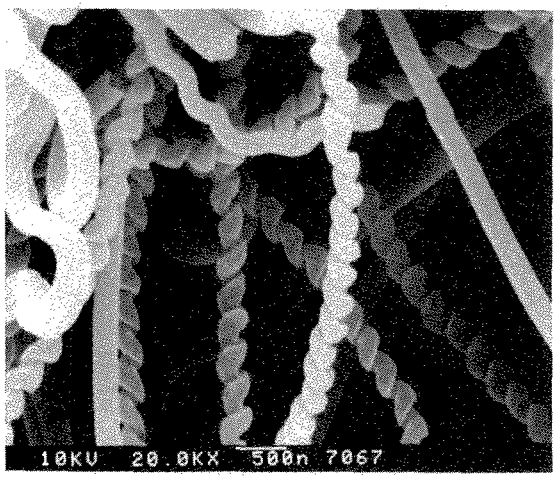

Fig. 4. Carbon nanocoils obtained by the application of magnetic field. Catalyst: Ni fine powder.

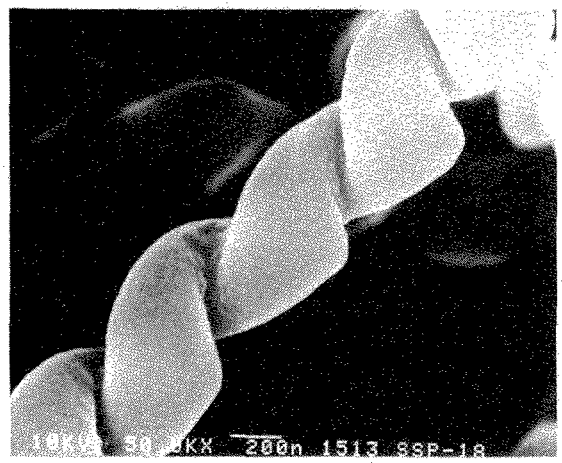

Fig. 5. An enlarged view of a carbon nanocoil,. Catalyst: Ni fine powder.

Using NiS powder as the catalyst, in which the flow rate of the impurity H_2S was reduced, because S was contained in the catalyst compound, which can decomposed to release sulfur, the twisted CNC were also obtained as shown in Fig.6, although the coil yield was less than that of Fig. 4. It can be seen that the CNC grown over Ni (Fig. 4a) and NiS (Fig. 6) catalyst are quite the same in the morphology and the dimension.

3.2 By other transitional metals, alloys or compounds catalyst

Various transitional pure metals were tried to prepare carbon nanocoils. Using Mo powder catalyst, the growth of small amount of the CNC with twisted form was observed among the straight carbon fibers (Fig. 7). Using Mo powder catalyst, the total carbon deposition amount was less than that using Ni or NiS catalyst. Further more, the twisted carbon nanocoils are less pure, because they co-grew together with thick carbon fibers and noodle-like carbon nanocoils. For another example, Using Cr powder catalyst, the growth of super-helix CNC with a coil diameter of about 500 nm and a super-helix diameter of 1.2 μm were sometimes observed among the straight CNC and irregularly bent carbon fibers as shown in Fig. 8.

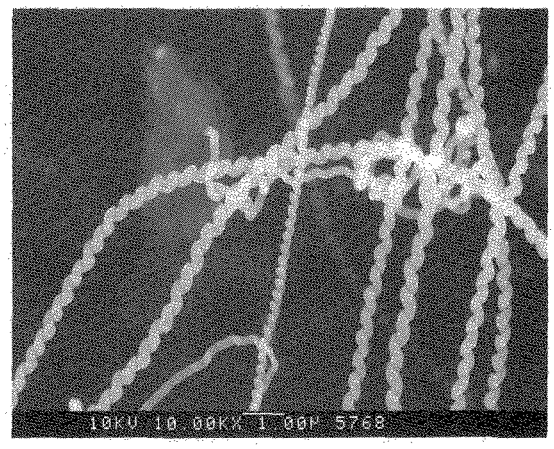

Fig. 6. Carbon nanocoils prepared by NiS catalyst

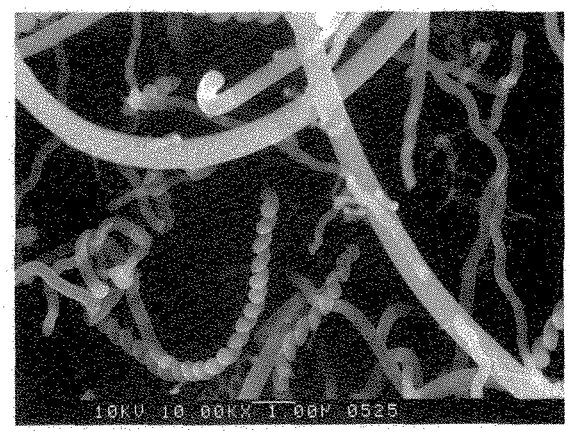

Fig. 7. Carbon nanofibers prepared by Mo catalyst.

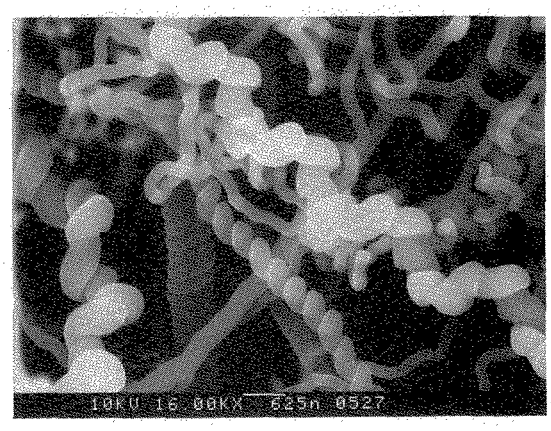

Fig. 8. Carbon nanofibers prepared by Cr catalyst.

However, using the alloys of above pure metals, Ni, Mo

and/or Cr, in additional Fe, that is, stainless steel, the CNC were synthesized effectively. Both Cr and Mo were very helpful for the effective preparation of the CNC. Using the stainless steel, it was found that large amount of CNC were formed on the surface of thick carbon fibers with a diameter of several μm as shown in Fig.9. The obtained CNC was generally twisted form with the same dimension with those described above, but the coil yield was servable times high. The catalyst grain was usually observed on the coil tip by pure metals as the catalysts. However, using Fe-based catalyst, such as stainless steel, the catalyst grain was sometimes observed in the middle part of the coils as shown in Fig. 10. It can be seen that the catalyst grain, which is a growing point of a fiber, present between the right-clockwise coiled CNC and left-clockwise-coiled CNC, as reported by S. Yang. et al. [8]. This growth pattern from the catalyst grain is different from that of the CMC carbon as reported by X. Chen et al. [9] If, these two coils entwine each other, double-helix coils may be formed.

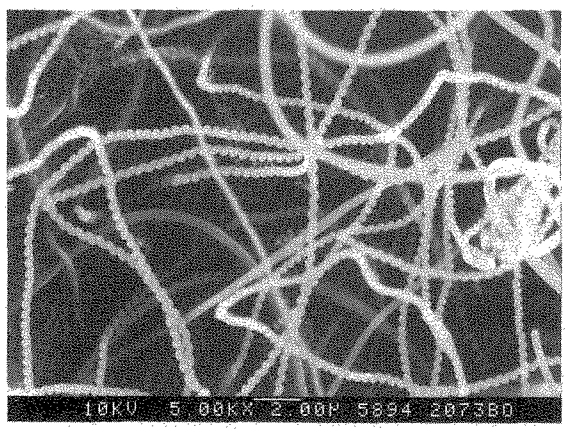

Fig. 9. Carbon nanocoils, by a stainless steel catalyst.

We have also found that by WS_2 catalysts, the growth of CNC with various morphologies such as a single-helix, a double-helix, and multiple-helix with inner coil diameter ranged form zero the servable micron were observed as shown in Fig. 11.

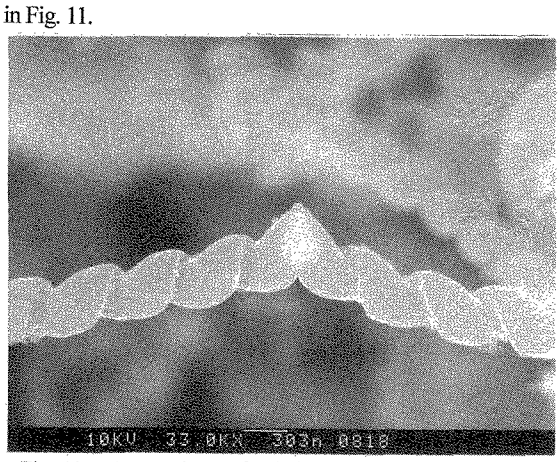

Fig. 10. A growth tip of twisting carbon nanocoils using a stainless steel as a catalyst.

4. CONCLUSIONS

By various metal and alloy catalyst, the CMC/CNC with various morphologies were obtained. Using stainless steel catalysts, a large amount of the single-helix CNC of a twisted-form were obtained. Furthermore, using WS_2 catalyst, multiple-helix CNC or single-helix CNC with dumbbell-type fiber cross-section as well as regular single-helix CNC could be obtained. It was considered that these morphological changes might be caused by the different shapes and catalytic activities of the catalyst grain.

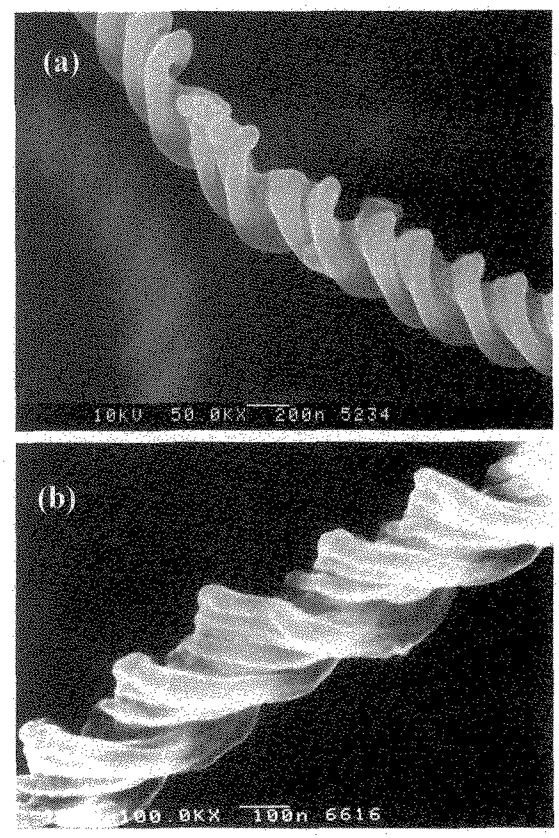

Fig. 11. Double-helix (a) and multiple- helix (b) carbon nanocoils. Catalyst: WS_2.

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