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Preparation and properties of carbon nanocoils by the catalytic pyrolysis of acetylene

S. Motojima, X. Chen, S. Yang, S. Shimada*, T. Hashishinand H. Iwanaga****

Department of Applied Chemistry, Faculty of Engineering, Gifu University, Gifu 502-1193, Japan
(e-mail:motojima@apchem.gifu-u.ac.jp) .
* Graduate School of Engineering, Hokkaido University, Sapporo 060-0813, Japan
** Faculty of Engineering, Nagasaki University, Nagasaki 852-8131, Japan

(Abstract) Carbon nanocoils with a 3D-helical/spiral structure and a coil diameter of several tens to several hundreds nanometers were prepared by the metal-catalyzed pyrolysis of acetylene. The preparation conditions, morphology, growth mechanism, microstructure and some properties were examined. Using fine powder of metals, ceramic powder-supported metals or sputtered metal thin films as the catalyst, carbon nanocoils as well as carbon microcoils were obtained. The carbon nanocoils are generally the single coils with a twisted form. The carbon coils can effectively absorb the magnetic wave of a GHz region.
Key words: chemical vapor deposition, vapor grown carbon fibers, carbon microcoils, carbon nanocoils, metal catalyst, coiling mechanism, heat-treatment, graphite nanocoils

1) Introduction:

Vapor grown carbon fibers (VGCF) are obtained by the catalytic pyrolysis of hydrocarbons and are used as the electrode materials, strengthened fibers in composites, etc. The carbon nanotubes is one of the VGCF and have unique crystallographic, physical and chemical properties. Accordingly, there has recently been growing interest in the preparation and characterization of the carbon nanotubes and also in the practical applications. Occasionally, during the preparation of carbon nanotubes or nanofibers by the catalytic pyrolysis of hydrocarbons, the growth of helical-coiled or spiral species has been obtained. Measured in nanometers, the coils diameters or coil pitch of these nanotubes or nanofibers range from tens to hundreds nanometer, while the diameter of the tubes or fibers forming the coils is smaller than these values. We call the helical/spiral coiled carbon tubes or fibers with a coil diameter less than one micrometer "carbon nanocoils", as opposed to the carbon microcoils with a coil diameter of several micrometers. The growth of these carbon nanocoils is generally accidental with poor reproducibility and low coil yield. Recently, we reviewed comprehensively the preparation and morphology ofthese carbon nanocoils[1].

We have prepared very regular carbon microcoils with good reproducibility and high coil yield by the catalytic pyrolysis of acetylene containing a small amount of sulfur compound, and examined the growth conditions, morphology, growth mechanism and some properties[2-5]. We also prepared carbon nanocoils using sputtered films of Au and Au/Ni[6]. Due to their characteristic coiling morphology and coiling-chirality, these carbon coils are expected to have many new and novel applications, such as electromagnetic wave absorbers, tunable devices (microsensors, microactuators, micromachines, etc.), field-electron emitters, chiral catalyst, etc.

In this study, the carbon nanocoils were obtained by the catalytic pyrolysis of acetylene using various fine powders of metals, ceramic powder-supported metals or sputtered metal thin films as the catalyst. The effect of catalyst on the growth and morphology of carbon nanocoils and their some properties were examined. We have found that the carbon nanocoils with a coil diameter of 100-500nm with various coiling morphologies could be obtained using different fine metal or alloy powders or fine films catalysts.

2) Experimental

A horizontal quartz tubes (30-60 mm i.d.), on the central part of which a vertical source gas inlet and gas outlet were attached, was used as a reaction tube. A schematic of the reaction tube is shown in Fig. 1. The reaction was carried out with the application of

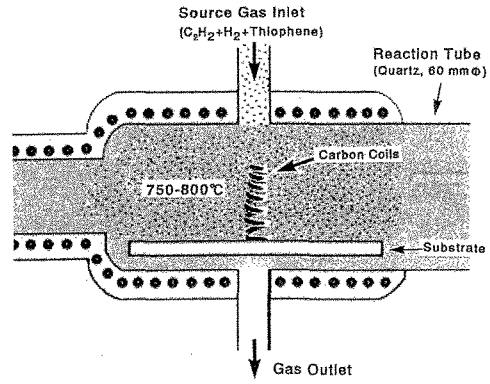

Fig. 1 Apparatus

the a.c. electromagnetic field emitted for the AC electric heater. A gas mixture of acetylene, hydrogen and hydrogen sulfide were introduced vertically onto the substrate surface on which catalyst was dispersed. The separation between the substrate and the source gas inlet tube was fixed in 10 mm. The gas flow rate of acetylene, hydrogen and hydrogen sulfide were 60-100 sccm, 200-400 sccm and 0.03-0.1 sccm, respectively. Reaction temperature was 600-850℃ and reaction time for 30 min. The used catalysts are as follows; 1) commercial fine metal powder, 2) ceramic powder-supported metals, in which fine ceramic powder of Al_2O_3, SiO_2, AN, etc. was mixed into metal chloride solution, stirred in ultrasonic waves, filtrated, dried, and calcinated in air at 770℃ for 2 h, 3) sputtered metal thin films. The obtained carbon

nanocoils was heat-treated at 2500℃ in a N_2 atmosphere for 5 h and then partially oxidized at 600℃ in air for 15 min. The absorption ability of the electromagnetic waves was obtained using the free-space microwave measurement system.

3) Results and Discussion

3.1) Catalysts: For obtaining carbon nanocoils, the size of a catalyst grain have to below several tens to several hundreds nanometer, because that the diameter of the fiber diameter, from which the coil is formed, is determined by the size of the used catalyst grain.

Using Ni fine powder (40-50nm diam.) as the catalyst at reaction temperatures 750-800℃, at which the maximum coil yield was obtained, the carbon nanocoils could not be obtained, while the carbon microcoils with a coil diameter of several microns preferentially grew. Fig. 2 shows the regular carbon

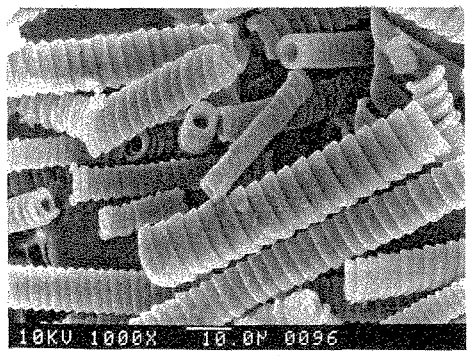

Fig. 2 Carbon microcoils (1)

microcoils with thick and rectangular fiber cross section. The coil diameter was 4-13 μ m while the catalyst grain was 40-50nm diam. This result may be caused by the easy sintering of fine Ni powder to form large grain size, and thus large fiber diameter resulting in the large coil diameter.

Using a Ni catalyst supported on the alumina powders, small amount of carbon nanocoils was obtained in mixing with straight and/or irregularly bent carbon nanofibers

Using an Au-Ni (Ni: 80mol%) catalyst supported on the alumina powders, large amount of carbon nanocoils could be obtained as shown in Fig. 3. The optimum reaction temperature for obtaining carbon nanocoils was 700-720℃. Furthermore, the optimum gas flow rate of acetylene and hydrogen sulfide was 60-90 sccm and 0.09-0.15 sccm, respectively. The content of nanocoils in deposits deceased with the increase of the reaction temperature while that of the straight carbon fibers increased. The deposits obtained at 770℃ was almost straight carbon fibers. The amount of the carbon nanocoils in the deposits decreased with increasing the Au content in the catalyst, and the Au-Ni (Au: 80 mol%) catalyst resulted in the formation of only straight carbon fibers. Using the Au catalyst supported on alumina powders or Au thin film catalyst sputter-deposited on alumina, graphite or BN plate substrate, no carbon nanocoil was obtained while straight carbon fibers grew. It is considered that the fine metal grain formed by the

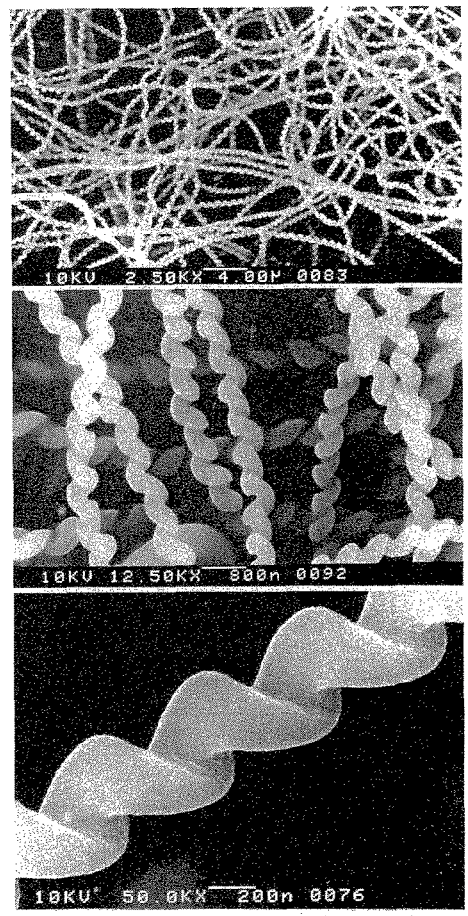

Fig. 3 Carbon nanocoils Catalyst: Au-Ni(Ni:80mol%)

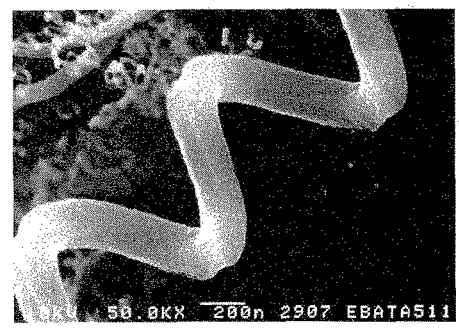

Fig.4 Extended spring-like coil.

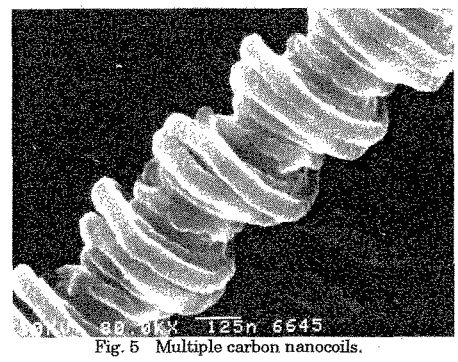

Fig. 5 Multiple carbon nanocoils.

calcinations of metal chloride, which was supported on the fine ceramic powder, is not sintered at high temperatures and form fine metal grains and thus thin carbon fibers. Above results suggest that the addition of small amount of Au metal in Ni catalyst results in the increase of an anisotropic property of the Ni catalyst, and results in the growth of thin fibers and thus thin carbon coils; carbon nanocoils.

3.2) Morphology and growth mechanism: Carbon nanocoil is usually a single coil with a twisted form as can be seen in Fig. 3. The single carbon nanocoils with spring-like form was also sometime obtained. Fig. 4 shows the extended spring-like single carbon nanocoils with the coil diameter 800 nm. Furthermore, various double or multiple coils are also sometimes obtained. Fig. 5 shows the multiple carbon nanocoils with the maximum coil diameter 500nm.

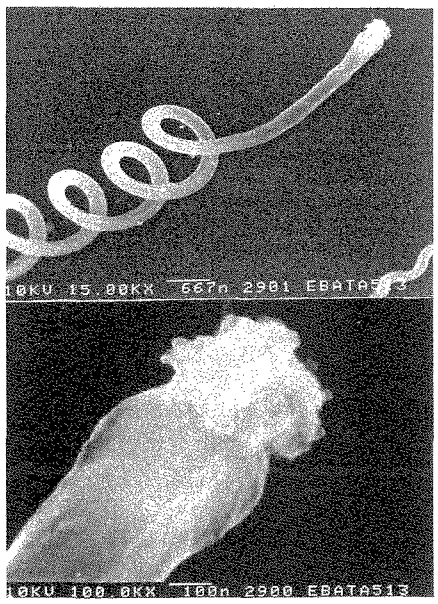

Fig. 6 Tip part of the carbon nanocoils.

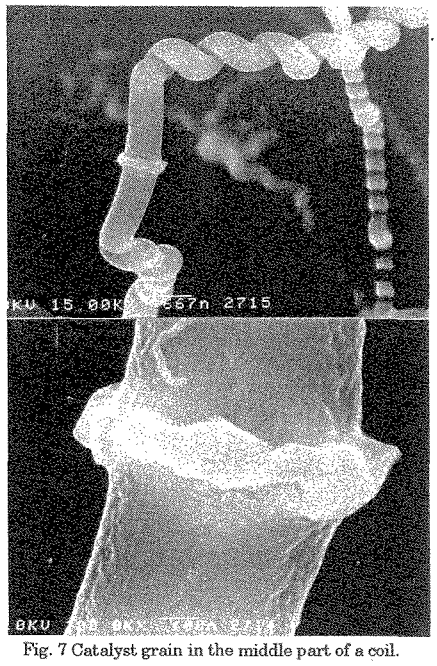

Fig. 7 Catalyst grain in the middle part of a coil.

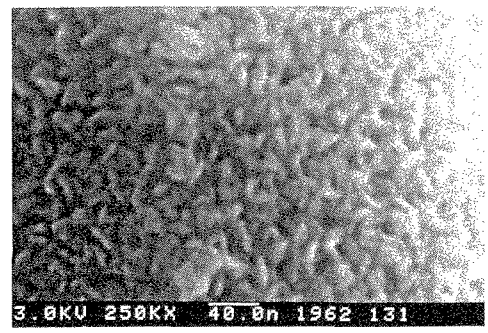

Fig. 8 Enlarged view of the surface of the carbon nanocoils

Fig. 6 shows the tip part of a single spring-like carbon nanocoils obtained using the Ni/Al_2O_3 catalyst. The presence of a Ni element in the tip catalyst grain was identified by the electron probe microanalysis. The catalyst was also sometimes observed in the middle part of a coil as shown in Fig. 7. The two fibers of the both side of the catalyst grain is a straight form of about 1 μ m length. The catalyst grain with many crystal facets extrude from the fiber surface. It is considered that these catalyst grains are a growing point of the carbon nanocoils and rotate by about a 60 rpm around the fiber axis. Accordingly, coiling or twisting direction of the two coils of both sides of the catalyst grain may be counter direction each other. Sometimes, continuous thin and fringe-like deposits can be seen in the inner rim (part) of the carbon nanocoils.

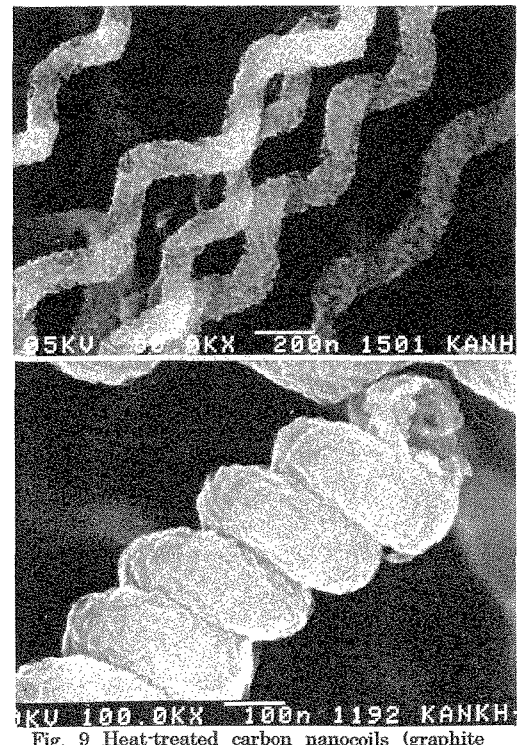

Fig. 9 Heat-treated carbon nanocoils (graphite coils)

3.3) Microstructure: Fig. 8 shows the enlarged view of the surface of the as-grown carbon coils. Fine grain of several tens length with irregular shapes can be seen. X-ray diffraction patterns, selected area electron diffraction patterns and Raman spectra of the

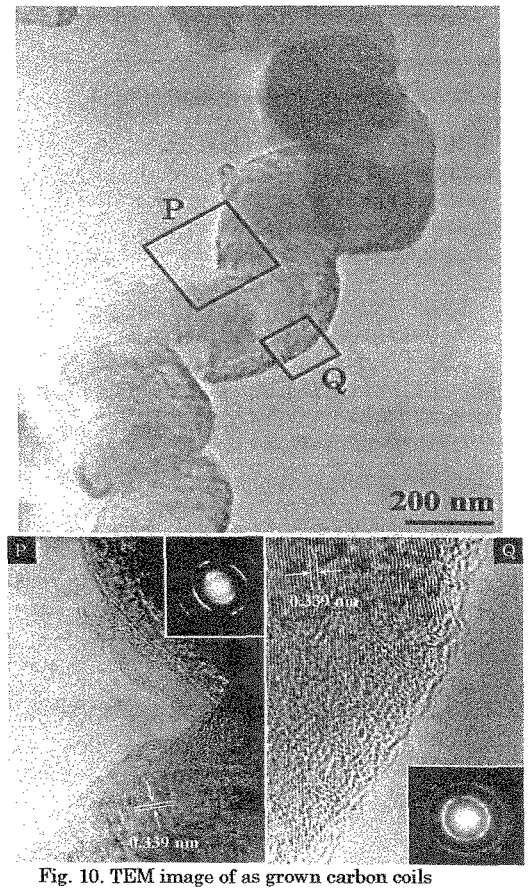

Fig. 10. TEM image of as grown carbon coils

as-grown carbon coils shows an amorphous state similar to that of the carbon microcoils.

It was observed that the carbon nancoils could be graphitized by the high temperature heat-treatment without changing coiling morphology while becoming slightly brittle. Fig. 9 shows the carbon nanocoils heat-treated at 2500°C for 5 hr in N_2 atmosphere. Growth of large grain of graphite can be seen on the surface.

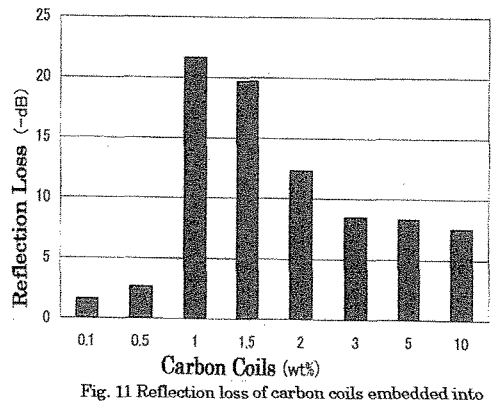

Fig. 11 Reflection loss of carbon coils embedded into polyurethane matrix

Fig. 10 shows the TEM image of the carbon nanocoils obtained by the heat-treatment at 2500°C for 5 hr in N_2 atmosphere. (P) and (Q) show the high resolution TEM images of the inner and outer part of the coils, respectively. The apparent contrast with 0.339 nm intervals, which decline 30-40° against the surface or fiber axis can be seen in both sides, indicating herring-bone structure, such as observed in the heat-treated carbon microcoils[7], can be seen. This d-value is slightly larger than that of the graphite.

3.4) Some properties

The carbon coils can effectively absorb the electromagnetic (EM) waves of GHz region according to Faraday` law. The absorption band depends on the size and chirality of the carbon coils, dielectric constant and thickness of a matrix, etc. It may be considered that the smaller the coil diameter, the higher absorption ability and higher absorption band region (high frequency) can be obtained.. Fig. 11 shows the reflection loss of the carbon coils embedded into a polyurethane matrix for a 75 GHz which will be used in an ITS (Intelligent Transportation System). The reflection loss of –20dB indicates the absorption ability of 99% of the irradiated EM waves and is a guideline of the practical applications. It can be seen that only 1~2 wt% addition of the carbon coils in polyurethane matrix results in the high reflection loss below –20dB, and that smaller or higher addition than 1~2 wt% results in the decrease of the reflection loss. The decrease of the reflection loss at higher addition of carbon coils in the matrix is caused by the higher reflection of the EM waves on the surface or bulk layers. On the other hand, the reflection loss of the ferrite or carbon powder in this band was only 0~-5dB.

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