# Vapor Phase Preparation and Some Properties of Carbon Micro-Coils (CMCs) †

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**Abstract**

*Carbon microcoils (CMCs) have an interesting 3D-helical/spiral form with a coil diameter of micrometer orders and a coil length of mm orders. Pulverized CMCs are generally embedded into polymer matrix to form CMC/polymer composites for various applications. The CMCs are very interested as a possible candidate for electromagnetic absorbers, remote microwave heating elements, microwave visualization materials, tactile and nearness sensors, chiral catalyst, etc. In this review, the preparation conditions, morphology, some properties and possible applications of the CMCs are briefly introduced.*

**Keywords**: Carbon microcoil, Ceramic microcoil, Acetylene, Tactile sensor, Electromagnetic absorber

## 1. Introduction

Materials with bulk, plate, thin films, powder, or straight fiber-like morphologies are now commonly available. However, Substances or materials with 3D-helical/spiral structure are not commercially available. Recently, the vapor growth of helical-coiled carbon nanotubes or nanofibers are reported and have attracting attentions in biotechnology and nanotechnology. Motojima and coworkers have prepared regularly coiled carbon fibers (carbon microcoils, "CMCs") with 3D-helical/spiral structures with high reproducibility and high coil yield, and the preparation conditions, microstructures, growth mechanisms, and some properties were intensively examined. These results are comprehensively introduced in reviews[1-3].

In this review, we will briefly introduce the preparation processes, morphologies, microstructures, and some properties of the CMCs and ceramic microcoils/microtubes. We also introduce the potential applications of the CMCs.

## 2. Preparation and morphology of carbon microcoils (CMCs)

The carbon microcoils (CMCs) is obtained by the catalytic pyrolysis of acetylene at 700-800℃. The CMCs grew vertically on the substrate surface on which catalyst powder was painted. On the other hand, the irregular CMCs with larger coil diameters and larger coil gap; super-elastic CMCs, than that of regular CMCs grew horizontally on the substrate surface. Using Fe-based alloys, Au, Pd/Pt, etc., as a catalyst, a single-helix CMC with large coil gap can be obtained. Under optimum reaction conditions, the purity or content of the CMCs in the deposits was almost 100%.The micro-coiling morphology of the CMCs is formed by the rotation of a catalyst grain that is exclusive growing point for the CMCs. The coiling (rotating) speed is about one cycle per second around the coil axis. The CMCs with various coiling morphology; regular coils, irregular coils, double

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coils, single coils, twist nanocoils, etc., can be obtained depending on the reaction conditions. Almost all of the CMCs are double-coiled forms in which two fibers entwine with each other such as the double helix structure of a DNA. The amount of the CMCs having right- and left-clockwise coiled forms are about the same. There are two forms of a carbon fiber cross section from which the CMC is formed; circular or elliptic-forms, and rectangular or ribbon-like-forms. We call the former coils as "circular-coils" and the latter coils as flat coils. **Fig. 1a** shows regular double-helix circular CMCs with a constant coil diameter of 5 $\mu$m and without any coil gap throughout one coil. **Fig. 1b** shows the regular double-helix flat CMCs with a constant coil diameter of 10 $\mu$m. The CMCs has generally high elasticity and can be extended up to 2-15 times original coil length and then elastically contracts to an original coil length, depending on the coil diameters, fiber diameters and cross section forms of carbon fibers from which coils is formed. Generally, the circular coils have higher elasticity than that of flat coils. **Fig. 2** shows the pulverized CMCs (CMC powder) with short coil length of 15-25 $\mu$m using a high speed smashing machine. The CMC powder is embedded into polymer matrix to form CMC/polymer composites of various forms of beads, sheets, filaments, etc., for various applications. It was found using XRD, Raman scattering, electron diffraction, and TEM examinations that the as-grown CMCs have almost amorphous structures comparable to that of activated carbon. It was also found that the as-grown CMCs can be graphitized by high temperature heat-treatment, and the graphite coils with herring born structure is obtained at above 2500℃ heat-treatment.

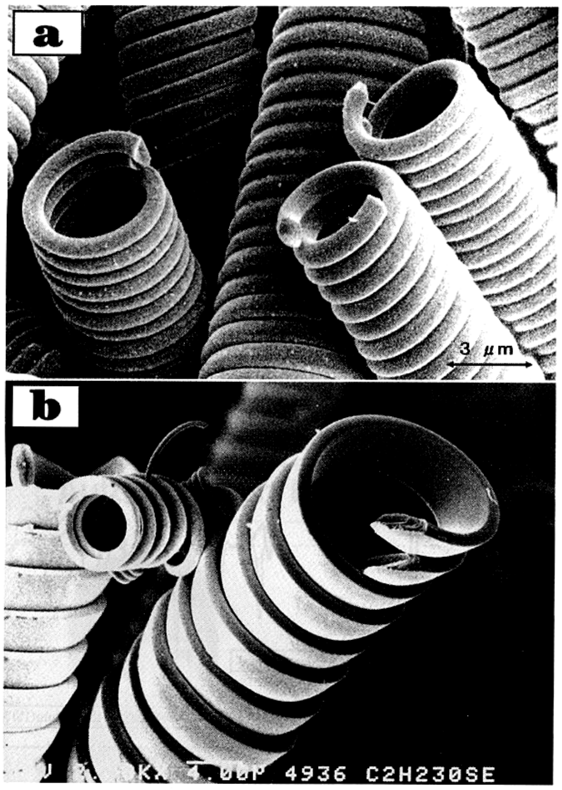


**Fig. 1** Rupture terminals of double-helix CMCs.
(a) Circular CMCs, (b) flat-CMCs.

### 3. Modification of CMCs to various ceramic coils

The as-grown CMCs can be easily vapor phase metallized and/or nitided to form micro-coils of metal carbides and nitrides with full preservation of the coiling morphology of the CMCs. Using very regular-coiled carbon coils without a coil gap, micro-tube of $MC_x$/C (carbon coil) /$MC_x$~$MC_x$ ($MC_x$: metal carbide) or $MN_x$/C/$MN_x$~$MN_x$ ($MN_x$: metal nitride) can be obtained. These modification processes is shown in **Fig. 3**. **Fig. 4** shows $TiO_2$ microcoils obtained by CVD coating of $TiO_2$ layers on the CMCs templates

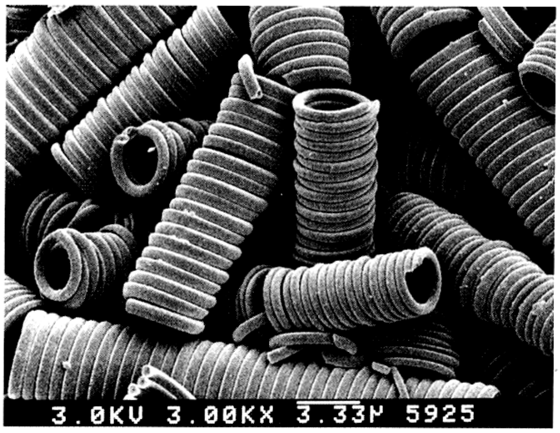


**Fig. 2** Pulverized CMCs (CMC powder) .

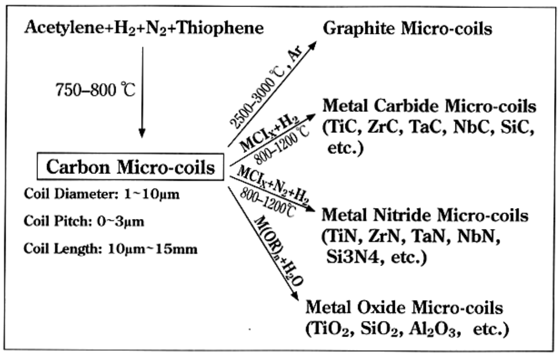


**Fig. 3** Modification process of CMCs to graphite coils and various ceramic coils/tubes.

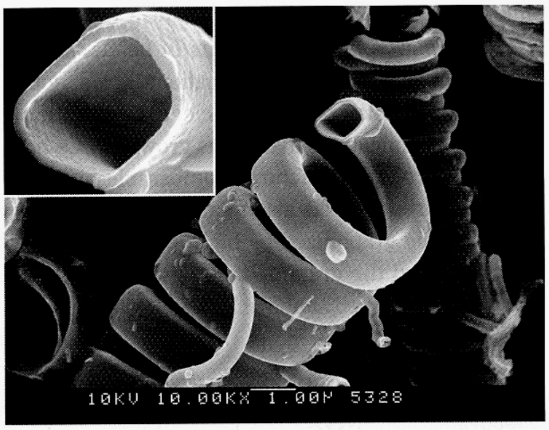


**Fig. 4** Coiled $TiO_2$ microtube obtained by a CVD coating of $TiO_2$ layers on CMC-template.

followed by oxidation process.

## 4. Properties

### 4.1 Composition and physical properties

The as-grown carbon coils is composed of 97.2~98.2 wt% C, 0.6~1.0 wt% O, 1.0~1.4 wt% H, 0.08~0.09 wt% S and 0.25 wt% Ni. **Table 1** shows density, specific surface area, and average pore size.

### 4.2 Electric Properties

The bulk (powder) electrical resistivity of the as-grown CMCs decreases with increasing the bulk density, and is 1-10 Ω · cm for 0.3 $g/cm^3$ and 0.1- 0.2 Ω · cm for 0.6 $g/cm^3$. The resistivity of the bulk carbon coils can be decreased steeply with the surface coating by carbon, TiC, TiN, ZrC, NbC, or TaC, but not by graphitizing at high temperature heat-treatment. The as-grown CMC can be easily elastically extended under small applied load. The electrical resistivity linearly increases by the extension and decreases by the contraction, probably caused by the formation of inner stress under the extension process.

### 4.3 Electromagnetic properties

It is reasonably considered that micro-coiling morphology of the CMCs is the most effective and ideal one for the generation of inductive current by Faraday's Law under the irradiation of electromagnetic (EM) wave resulting in effective absorption of EM wave. **Fig. 5** shows the reflection loss of EM waves of 10-110 GHz region by the CMC (1wt%) /PMMA foamed plate. It can be seen that the reflection loss shows above -20 dB (above 99 % absorption) at wide frequency ranges of 50-110 GHz. These results indicate that the carbon coils is a promising candidate as a novel EM absorber, especially in the GHz range, because of its micro-coiling morphology. The thin sheet containing CMCs (10 wt%) /PMMA beads was heated in a microwave oven (2.45 GHz) and the heat increase by the absorption of EM waves were measured by a IR thermography. It was observed that the temperature increased at each separations of 60 mm from the right side, and no temperature increases was observed between them. The separation was responsible to a half wavelength of 2.45 GHz. That is, microwave and their distribution within a microwave oven can be visualized by CMCs sheets, while the EM wave cannot be observed by naked eyes.

### 4.4 Chemical properties

The carbon coil becomes oxidize at about 450℃ in air, and the weight significantly decreased with increasing temperature and burn out at 700℃ . On the other hand, the graphite micro-coils obtained by the

**Table 1** Density, specific surface area an pore diameter of the as-grown carbon coils

| External EM field (AC, 60 Hz) | Bias valtage (V) | Density ($g/cm^3$) | Specific surface area ($m^3/g$) | Pore dismenter (nm) |
|---|---|---|---|---|
| *with* | without | 1,7234 | 100-140 | 3~4 |
| | DC650 | 1,8398 | | |
| | | 1,8019 | | |
| | AC1300 | 1,7431 | | |
| *without* | without | 1,7431 | 70-130 | 3~4 |
| | DC 650 | 1,7978 | | |
| | AC1300 | 1,7901 | | |
| *Ref.* | nanotubo | | | |
| *(carbon filters)* | VGCF | 2,0817 | 20-30 | |
| | PAN | 1,7402 | 2-10 | |
| | Pitch | 2,0154 | 1-10 | |

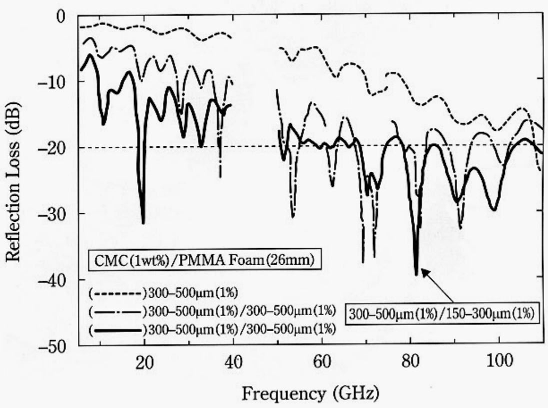


**Fig. 5** Reflection loss of CMC (1wt%) /PMMA foam.

heat treatment of as-grown carbon coils at 3000℃ for 6 hrs in $CO+CO_2$ becomes oxidize at about 700℃ in air.

### 4.5 Bio-activation properties

The highly-purified as-grown CMCs were added in skin cell (Pam 212) and collagen (mRNA) and the propagation or activation effect of CMCs were examined. It was observed that the skin cell formation was promoted by 160% versus control (without addition of CMCs) by the 1000 ng/ml addition. The collagen formation was also increased by 1.14 times versus control by the 1000 ng/ml addition. These results suggest that the CMCs can effectively activate the cell propagation. Accordingly, as-grown CMCs are commercialized as an additive in cosmetics.

### 4.6 Tactile and nearness sensing properties

The CMCs have high elasticity and can be easily extended and contracted under small applied loads. It was found that electrical parameters such as resistivity (R), inductance (L), capacitance (C), impedance (Z), phase angle ($\theta$) changed under the extension or contraction. The elastic CMCs was uniformly embedded into elastic polysilicone, and the change in electrical parameters were examined under applied small loads. **Fig. 6** shows the change in L parameter of the CMC (1wt%)/ polysilicone elements under applied load. It can be seen that the large change in L signal under applied 1mgf is observed, and the signal strength increases with increasing applied load. The change in electrical parameters was also observed in accessing of some substances. That is, the CMC/ polysilicone elements have high tactile and nearness sensing property comparable to human skin, and the detection limit is below 1mgf (ca.1Pa).

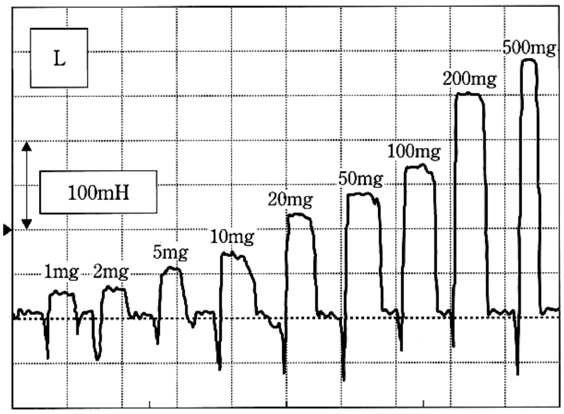


**Fig. 6** Change in L (inductance) parameter of CMC (1wt%) thin sensor element under applied load.
Thickness of element: 0.1 mm.

### 5. Conclusions

Carbon microcoils (CMCs) have an interesting 3D-helical/spiral form with a coil diameter of micrometer orders and a coil length of mm orders. The CMCs can be easily pulverized without rupturing their coiling morphologies. The pulverized CMCs are generally embedded into polymer matrix to form CMC/polymer composites for using in various applications. The CMCs and ceramic microcoils have many novel functionalities, and are very interested as a possible candidate for electromagnetic absorbers, remote microwave heating elements, microwave visualization materials, hydrogen absorber, field emitter, micro sensors, chiral catalyst, capacitors, energy converters, etc.

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## Author's short biography

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Dr. Xiuqin Chen received M.E. degree from Xiamen University, China in 1987. She was promoted to a professor of Huaqiao University, China in 2000. She received a Ph. D. degree from a Gifu University in 2000. She served at Gifu University as an invited researcher in 2001, a postdoctoral fellowship for foreign researchers of JSPS (2002-2004), and a special researcher of Gifu University (2005~).

## Author's short biography

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Seiji Motojima In 1977, he received the Ph. D. degree from the Nagoya University. He became an assistant professor in 1971, associate professor in 1982, and professor in 1990 at Gifu University. He has received several awards for his research excellence from various societies, such as The Chemical Society of Japan, The Ministry of Education, Culture, Sports, Science and Technology, The Jpn, Res. Ins. Mater. Technol., Port for Techno-Democracy, etc. His current research focus is creation and characterization of 3D-helical/spiral materials, especially of carbon microcoils (CMC) with novel functions.