Novel Functional Materials --Carbon Microcoils/(CMC)--

Properties and Potential Application

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Prologue to selendipitic discovery of silicon nitride microcoils and carbon microcoils -------Beautiful face of ceramic single crystals obtained from high corrosive atmosphere using CVD process------

- Reaction temperature: 800~2500°C
- Corrosive atmosphere: HCl, H₂S, etc
- Crystal size: 10~500 µ m

Golden prizes got in the Micrograph Exhibition for Ceramics Crystals (Ceramic Society of Japan)











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What is CMC (Carbon microcoils) ?

- 1) A kind of vapor grown carbon fiber (VGCF)
- 2) Preparation process: by metal catalyst-activated CVD
 - Carbon source: acetylene (for weld)
 - -Catalyst: Ni, Fe-Ni, etc.
 - •Reaction temperature: 750-800°C
- 3) Morphology:3D-Helical/spiral structure
- 4) Dimension: •Coil diameter: ~μm
 •Coil Length ~10mm
- 5) Microstructure: Amorphous
- 6) Characteristics: •Coiling-chirality
 - •High-elasticity
 - High interaction with microwaves

Critical difference of CMC from carbon nanotube

	CMC	CNT
Morphology	3D-helical/spiral	Straight
Dimension	Coil diam: ~μm Fiber diam:0.01~0.5μm	- ~nm
Crystallinity	Amorphous	Crystalline
Pore in the fiber axis	noné	Tube-like pore
Interaction with microwave	high	none





Double-helix Carbon Microcoils(CMC)



Double-helix carbon microcoil (flat-type)



Commercially available representative CMC

4936 C2H230SE

Regular Right-hand Carbon Microcoils

Regular left-hand Carbon Microcoils





CMCs with various interesting morphologies (**2**)





Twinned single-helix CMC grown from a catalyst grain

Arrow indicate a catalyst grain







Super-helix CMC

Super-helix carbon nanocoils (Catalyst: Fe, 700 °C)



4.00KX 2.50M 7018

20KV



Cover photographs of Journals



Volume 39 : Number 8 : 15 April 2004 JMTSAS 39(8) 2645-2972 (2004)



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These interesting micrographs were published as cover photographs of international journals.







NORTH HOLLAND http://www.elsevier.com/locate











Microstructure of as-grown CMC



XRD patterns (left) and Neutron diffraction analysis (right) of as-grown CMC and heat-treated CMC in CO+CO₂ or Ar atmosphere





Influence of heat-treatment temperature on the spring constant



Videos showing the extension and contraction of as-grown CMC









Mechanical stability of CMC

Characterization process

CMC (0.3g)/1,2-Dichloroethane(60ml) stirred by magnetic stirrer in conical beaker (100ml) for 6 days









Another important characteristics of CMC is changing in electrical parameters under the extension or contraction of the coils. This figure shows the relationship between the extension and electrical resistivity.

It can be seen that the electrical resistivity increases with the extension and decrease with the contraction. Other electrical parameter, such as L, C, Z, θ also changes by the extension or contraction.





Fig. 2. Temperature dependence of the resistance for the as-grown coil

Influence of coil diameter and fiber diameter on the spring constant of asgrown CMC



Characteristics and Properties of the Carbon Micro-coils

Morphology : Double Helix Coil Diameter : 1-10 µm Coil Pitch : $0.01-5 \mu m$ Coil Length : 0.1-10 mm Fiber Diameter : 0.01-1 µm Elasticity (Extension Ratio) : <u>1.5-10 times</u> Chemical Composition (wt%) : C=97.5-98.2 H=1.0-1.4S=0.03-0.09 Crystallographic structure : Amorphous Density : 1.81-1.88 g/cm : <u>100-140 m²/g</u> Specific Surface Area Specific Electrical Resistivity : 10-0.1 Ωcm Thermal Conductivity (Bulk) 0.0446 W/m/k (for 0.0884 g/cm³) 0.0562 W/m/k (for 0.2055 g/cm³)

Interaction of CMC with EM wave

CMC with 3D-Helical/spiral form

Electromagnetic (EM) Wave

Generation of inductive electromotive force → electric current → Joule`s Heat

Faraday's Law of Electromagnetic Induction

カーボンマイクロコイルに電磁波が当たるとコイル内に 誘導起電流が流れジュール熱が発生し熱エネルギーに 変わる



Fig. 2. Schematic of an apparatus used for the measurement of electromagnetic induction of the CMC in a static magnetic field.

Generation of inductive electromotive force


Application to magnetic sensor element

Relationship between magneto-resistance and magnetic field of a piece of CMC.



Fig. 5. Field direction dependence of magnetoresistance measured at 300 K (a) for the as-grown coil and the coils annealed at $1500 \text{ and} 2000 \text{ }^{\circ}\text{C}$, and (b) for the coils annealed at $2500 \text{ and} 3000 \text{ }^{\circ}\text{C}$.





Application to laser sensor



Application to field emitter





Potential application in micro antenna

Micro antenna of various types are prepared.





Characteristics of micro-antenna for space development 10 11.5GHz 0 13.5GHz 320 310 -10 300 Gain[dBi 290 -20 280 270 -30 260 100 リード線(比較用) 250 110 -40CMCAT-001 240 CMCAT-002 230 CMCAT-003 220 -50CMCAT-004 200 160 70 190 **Radiation pattern** -601.0 **Gain ratio** 30.0 [GHz] 10.0 共試体 ホーンアンテナ ホーンアンテナ 試供体 ネットワーク パソコン等 **1** 波吸収体

Measurement/evaluation system

CMC Technology Development Co., Ltd.

ネットワーク アナライザー

ターンテーブル

CMC-Containing Fibers



CMC-keratin cloth

CMC(3wt%)/PET fibers



Characteristics of CMC as reinforcing fibers

Stress-strain diagram of CMC/Epoxy resin(Young's modulus:700MPa)composite



	Tensile strength (MPa)	Stretch (%)	Young's modulus (MPa)
Blank	42	65	690
Carbon fiber (3wt%)	44	67	750
CMC 3wt%	40	51	720

(n=3)

Straight carbon fiber composite

Tensile strength, Stretch and Young's modulus: slightly increased

CMC composite

- Tensile strength: slightly decreased
- Stretch, Young's modulus: slightly increased

Stress-strain diagram of CMC/Epoxy resin (Young's modulus:1MPa) composite



	Tensile strength (MPa)	Stretch (%)	Young's modulus (MPa)
Blank	0.36	614	1.2
	(σ=0.035)	(<i>σ</i> =36)	(<i>σ</i> =0.12)
Carbon fiber	0.56	714	1.4
(3wt%)	(σ=0.031)	(σ=61)	(<i>σ</i> =0.13)
CMC	0.83	605	2.1
(3wt%)	(σ=0.034)	(σ=16)	(σ=0.37)

Straight carbon fiber composite

Tensile strength, extension and Young's modulus: slightly increased

CMC composite

Tensile strength, Young's modulus: increased by ca. 2 times







High microwave absorption property of CMC is now applied in a microwave oven crucible. That is, the CMC was embedded into ceramic crucible, and the crucible was heated for 10 min in microwave oven. The highest temperature was attained up to 1200°C









Application to cosmetics



Breeding effects of CMC on skin cells and collagen fibrils

This figure shows the effect of CMCs on the skin cell and collagens breeding. It can be seen that the number of skin cell; Pam 212, increases by 160% by the addition of CMC of 1000ng/ml, against a control sample, that is, without addition of CMC. In the case of collagen fibrous too, breeding effect of the addition of CMC was observed.



成分:〈モイストタイプ〉ポリアクリル酸アルキル、イソノナン酸イソトリデシル、メチルフェニルポリシロキサン、ミネラルオイル、トリ(カプ リル・カプリン酸)グリセリン、パラフィン、硫酸Ba、ポリエチレン、メトキシケイヒ酸オクチル、ポリアクリル酸メチル、セスキオレイン酸ソ ルビタン、霊芝エキス(黒霊芝、赤霊芝)、加水分解コラーゲン、炭素(カーボンマイクロコイル)、ビタミンAパルミテート、ビタミンE、ビタ ミンCリン酸マグネシウム、メチコン、BG、精製水、オレスー3リン酸、香料、マイカ、酸化チタン、酸化鉄

使ハドフ薬(図)

成分:〈パウダータイプ〉セリサイト、(タルク/ケイフッ化K)焼成物、窒化ホウ素、合成金雲母、ポリアクリル酸メチル、タルク、ジメチコン、 メトキシケイヒ酸オクチル、マイカ、シリカ、コハク酸ジオクチル、(ジメチコン/ビニルジメチコン/メチコン)クロスポリマー、霊芝エキス (黒霊芝、赤霊芝)、加水分解コラーゲン、炭素(カーボンマイクロコイル)、パーフルオロカプリリルトリエトキシシリルエチルメチコン、ビタ ミンAパルミテート、ビタミンE、ビタミンCリン酸マクネシウム、ポリクオタニウムー61、メチコン、BG、精製水、ステアリン酸亜鉛、パラ ベン、香料、酸化チタン、酸化鉄

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Effect of CMCs for anti-breeding of Hela cell (human-uterus-neck-cancercell) (CMC : 0.04 wt%)



Applicable as cancer remedy medicine



This figure shows the effect of CMC on the breeding of cancer cell. When the CMC was added by 0.04 wt%, the number of cancer cell after 7 day breeding is about 20% against control sample.

That is, the CMC can be applicable as a cancer remedy medicine.

Why CMC is affective for the recovery of skin cell or for cancer remedy is not known yet.

Application to electro microwave absorber



Free space microwave measurement system (JFCC-HVS)





CMC+Microballoon+Al flake+Carbon Fiber+Carbon black











Change in electrical resistivity of CMC/polysilicone composite sheet in relation with the addition amount of CMC



Change in electrical resistivity of composites under applying compression stress of 0.1~0.2MPa)



Change in electrical resistivity of composites under applying compression stress



Model of various receptors of human skin (by Prof. T. Maeno of Keio Univ.)

Finger Prints

- 1) Meissner's corpuscle is a helical receptor of cocoon-like forms, which is formed by the coiling of the terminal of nerves fibers.
- 2) Meissnor's corpuscles are present in two arrays under finger prints with the density of 1500/cm³.
- 3) Meissnor's corpuscles shows a high sensitivity and discrimination ability to applied physical stimuli.



- Human skin has very high sensitivity and discrimination ability to various stresses and stimuli, such as, mechanical loading, pressing, picking, sticking, rubbing, temperature, sound, etc.
- So, It is expected that if CMC is embedded into elastic rubbers, high tactile sensing and discrimination ability corresponding to that of human skin may be obtained.
- According to this concept, we have prepared artificial skin with tactile sensing properties. These sensor elements were made of CMC and elastic polysilicone rubber composite sheet.
- So, it is expected that if CMC is embedded into elastic rubbers, high tactile sensing and discrimination ability comparable to that of human skin may be obtained.
- •According to this concept, we have prepared artificial skin with tactile sensing properties. These sensor elements were made of CMC and elastic polysilicone rubber composite sheet.



Meissner's Corpuscles

- 3D helical-coiled nerve fibers (Proteins)
- Single-helix ?
- Diameter of helix : 40-70 μ m
- Length of helix : 20-150 μ m

Carbon Microcoils (CMC)

- •3D helical-coiled carbon fibers (Pure carbon)
- Double-helic or single-helix
- Diameter of coils : 1-20 μm
 Coil Length : 50-500 μm

Relationship between Meissner's corpuscle and carbon micorcoils

There are many similarity between Meissner's corpuscle and carbon microcoils in the point of conformation and size

Structure of CMC Sensor element



The CMC sensor element have a very simple structure, composite of CMC and elastic matrix, and can be easily miniaturizing by cutting successively the large sheets to small sheets or blocks by using conventional cutter or ultrasonic cutter. The minimum size of obtained sensor element was about 100x80x80mm³



Change in LCR parameters of micro-sensor (100x100x100

μ m³)

Matrix: Elastic silicone resin Coil Length: $500-500 \,\mu$ m Coil Diameter: $1-10 \,\mu$ m Addition amount: 5wt%Load: 0.5gf









The CMC sensor element has proximity sensing property as well as tactile sensing property



Change in LCR parameters under approaching a hand to CMC sensor element



SCALE

200 \$

LS

R

500 uH/div REF 100 g/div REF -88.5 mH

Change in impedance (z) of the CMC sensor element under approaching and touching to a Cu plate CMC1% (電極間2mm) CMC(1wt%)/polysilicone 200KHz Z/Z Distance between CMC sensor element and Cu plate

Effect of target substances on the change in impedance



Influence of the area of target object on the gain of proximity signal



CMS was dispersed uniformly in the matrix, while the CMC did not form a percolation structure (electrical contact). en to tabe fit ce fe to 11



Possible proximity sensing mechanism of CMC sensor element (Changing in space capacitance by accessing conductive substances)



Applications to medical instruments for low invasive surgery





Application to the advanced medical instruments



X-ray Diagnostic Instruments

Application to safety rotary door or elevator's door



Red line indicates CMC sensor element



CMC/Polyurethane fibers







Preparation of Ceramic Microcoils/microtubes using CMC as a Template (by the high temperature vapor phase diffusion process)



TiC/CMC Microcoils





TiO₂ microcoil



10KV 10.00KX 1.00M 5328

Application of Carbon Microcoils

1	Electromagnetic	(1) Beads			
	absorbers	(2) Foams			
		(3) Ceramic beads			
		(4) Super-thin EM absorbers			
2	Tactile sensors	(1) Medical sensors			
		(2) Humanoid robot sensors			
		(3) Artificial skins with tactile			
		sensing properties			
		(4) Aerospace sensors			
		(5) Industrial sensors			
3	Bio-activators	(1) Breeding or activating			
		catalysts for skin cells,			
		collagen fibrils,			
		microorganisms, etc.			
		(2) Activators of metabolism			
		(3) Tissue engineering			
4	Micro-antenna	(1) Micro-antenna for aerospace			
		(2) Energy converters			
5	Remote-heaters	(1) Remote micro-heaters			
		(2) Micro-heaters for DDS			
6	Others	(1) Super-elastic conductors			
		(2) CMC containing fibers			
		(3) etc.			





Side-view of CMC (arrow: Ni₃C single crystal)





Table 4. Effects of Ni catalysts (single- and poly-crystals) on the deposition rate of total carbon and coil yield

Catalysts	Ni single-crystal plate			Ni poly-crystal plate
	Ni(100)	Ni(111)	Ni(110)	
Deposition rate of total carbon (mg/cm ²) Coil Yield (mol%)	32 10.2	23 6.7	19 3.2	23 4.8

Coiling mechanism based on the anisotropic property of catalyst grain

