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The 62th CerSJ Awards for Academic Achievement in Ceramic Science and Technology: Review

Development of ceramic microcoils with 3D-herical/ spiral structures

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Various modified CVD processes, such as modified hot filament method, vapor phase diffusion process, in-situ CVD process, catalytic CVD process, for the preparation of ceramics single crystals and fibers were developed. The preparation conditions, morphologies, microstructure and properties of transition metal carbides, nitrides, borides, silicides, sulfides, etc were examined. We have first found that various ceramic fibers with 3D-helical/spiral structure, such as Si_3N_4, carbon, TiC, TiO_2, etc. were obtained using metal-catalyzed CVD and/or vapor phase diffusion processes under critically controlled reaction conditions. Carbon microcoils (CMC) with double-helical structure were obtained with high reproducibility by metal catalyzed pyrolysis of acetylene. The CMCs have many interesting and eminent characteristics, such as 3D-helical/spiral microstructure with μm orders in coil diameters, diverse microstructures from amorphous to graphite structure, changing in electrical parameters under the application of various stimuli, high microwave absorption and microwave heating abilities, breeding or anti-breeding effect on cells, fibrils of organisms, etc.

Key-words : CVD, Single crystal, Carbon microcoil, Helical substance, Electromagnetic wave absorber, Tactile sensor

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1. Introduction

Chemical vapor deposition (CVD) is a very useful technique by which thin films, such as epitaxial layers, passivation layers, hard coating, corrosion protective coating, optical coatings, whiskers, fibers, and bulk single crystals are prepared on various substrate including flat surfaces, filaments, and powder. Accordingly, CVD gains a firm position as a key technology for the preparation of semiconductor devices, optical fibers, coated tools, and other technological products. The preparation of single crystals is very important for examining and characterizing the basic crystallographic, physical and chemical properties of compounds. Many crystal growth methods, such as the floating zone method, Bridgeman's method, Bernuil's method, Czochralski's method, CVT, and CVD have been developed. Among these methods, CVD is the promising candidate for obtaining single crystals with various morphologies, such as bulk crystals, thin films, whiskers, as well as other interesting shaped crystals, such as 3D-helical/spiral forms because of using an unrestricted gaseous atmosphere.

We have developed a modified hot filament method for the preparation of large bulk crystals of transition metal carbides, nitrides, silicides and borides.[1)] We have also developed a "diffusion process" and "in-situ CVD process" as modified CVD processes for obtaining single crystals with interesting morphologies of iron metal group compounds.[1)] We have found that using metal catalyzed CVD processes and/or vapor phase diffusion processes various ceramic fibers with 3D-helical/spiral structure, such as silicon carbide, silicon nitride, carbon, etc. were obtained under critically controlled reaction conditions.[2)–5)]

In this work, various ceramic crystals or fibers with interesting morphologies, especially with 3D-helical/spiral structure were obtained, and the preparation conditions, morphologies, microstructure, growth mechanism and some properties were examined.

2. Results and discussion

2.1 Preparation and characterization of interstitial compound crystals by modified hot filament CVD process

Among many interstitial compounds, crystal growth of titanium carbide (TiC) has been the most intensively investigated by using many growth processes. We have obtained the TiC bulk crystals of $5 \times 5 \times 10$ mm^3 from a gas mixture of $TiCl_4$, n-C_3H_8 (or C_6H_6 or CCl_4), H_2 at 1700–1800°C using modified hot filament CVD process.[6)] Single crystals of titanium diboride (TiB_2) were obtained from a gas mixture of $TiCl_4$, BCl_3, H_2, and Ar on a Ta wire twisted around a Ta filament in which gas flow ratios [BCl_3/$TiCl_4$] was fixed at 1/2. We have found that, without addition of hydrogen chloride to the growing atmosphere, well-formed single crystals of TiB_2 were not obtained at any growth conditions; addition of hydrogen chloride was essential for the growth of well-formed TiB_2 single crystals.[7)] **Figure 1** shows well-formed hexagonal plate-like TiB_2 crystals with mirror-like faces at 1935°C with the addition of hydrogen chloride of 20 vol% in a source gas. The largest crystals obtained were about 5 mm across and 0.1 mm thickness for a 2 h reaction time.

2.2 Crystal growth by a diffusion process and in-situ CVD process

Vapor phase diffusion treatment of metal in which light elements such as C, B, or N are diffused into metals at high temperatures to form the layers of carbides, borides or nitrides have been commercially used as a surface treatment of metals to obtain wear and/or corrosion resistant surfaces. Generally, very dense and adherent coating layers are formed on the substrate

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Fig. 1. TiB_2 single crystals obtained by modified hot-filament process. reaction temperature: 1935°C.

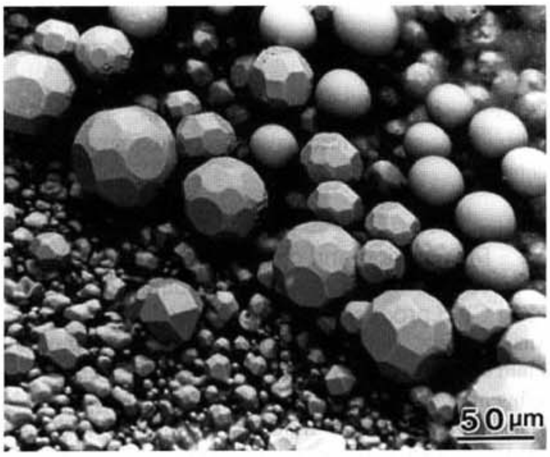

Fig. 2. $FeSi_2$ single crystals obtained by diffusion process. reaction temperature: 1100°C.

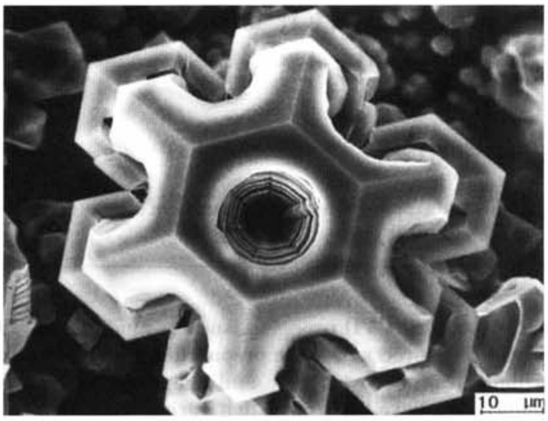

Fig. 3. CrB_2 single crystals with concentric hollows. reaction temperature: 1050°C.

surface by the diffusion treatment. It was found that if the diffusion velocity of metal atoms of substrate through the deposited layers is larger than that of diffused atoms from vapor phase, single crystals grow on the surface without forming dense diffusion layers. For example, well-formed $FeSi_2$ single crystals of various morphologies, such as polyhedral, golf ball-like, or egg-like has been obtained by the siliconizing of iron plate using $Si_2Cl_6 + H_2$ gas mixture at 1100°C as shown in **Fig. 2**.[8] Chromium diboride (CrB_2, hexagonal) crystals were obtained from a gas mixture of $CrCl_2$, BCl_3, H_2 and Ar at 1050–1100°C on a graphite substrate.[9] Hexagonal plate-like crystals of CrB_2 grew among polycrystallites. The maximum size of the CrB_2 crystals obtained was 6 mm in diagonal and 0.1 mm in thickness. **Figure 3** shows a well-formed regular hexagonal CrB_2 crystal with a beautiful concentric hollow region in the central part of the hexagonal face. The formation of the hollow region is probably caused by deficient mass transport through the gaseous laminar film. Crystals with interesting 3D-helical forms were obtained using the diffusion process or in-situ CVD process. These crystals are shown next section.

2.3 Crystal growth with 3D-helical structure

It was found that the new ternary crystals with interesting 3D-helical/spiral forms of $(Cr_{1-x}Fe_x)_5Si_3$ (hexagonal) were obtained by the siliconizing of SUS 410 (Cr 13%) plate.[10] These compound crystals have also been obtained by the siliconizing of other stainless steel (SUS 302, Cr 18%, Ni 8%; SUS 310, Cr 25%, Ni 20%.[11), 12)] The composition of the crystals obtained was estimated to be $(Cr_{0.23}Fe_{0.77})_5Si_3$.[11] It was very interesting to note that nickel was not observed at all in the crystals, even though large amount of nickel were contained in the substrate. Ni does not form Ni_5Si_3 the way Fe and Cr do. The reason is not understood yet. The new ternary compounds of $(Cr_{1-x}Fe_x)_5Si_3$ were far more stable to concentrated hydrochloric acid solution than that of high nickel stainless steel (SUS 302 or 310).

We have found that the new ternary compound crystals of $(Cr_{1-x}Fe_x)_5Si_3$ have also obtained on an inner wall of a quartz boat by the "in-situ CVD process" using in-situ reaction of stainless steel (SUS 410) powder, Si_2Cl_6 and H_2 at 1100°C.[13] Using the in-situ CVD process, the crystals with various interesting morphologies, such as fibroid, seaweed-like, spiral, conical, rose-like, and globefish-like have been obtained. **Figure 4**(a) shows the well-formed spiral crystals in which one of the prismatic faces was spiraled hexagonally by three times toward the inside.[14] These spiral crystals first grew conically up to about 20–30 μm in height and then grew hexagonally. Figure 4(b) shows double-spiraled rose-like crystals.

Zirconium disulfide (ZrS_2) crystallizes in the CdI_2 structure, and yielding generally plate-like crystals. We have found that anomalous pillar-shaped ZrS_2 crystals, which were abnormal in the sense that the whole lateral surface was an (0001) plane, grew among platelet colony from a gas mixture of $ZrCl_4$, H_2S, H_2 and Ar on a quart substrate at 850°C.[15] The pillar-shaped crystals grew preferably at gas flow rate of $S/(Zr + S) = 0.7–0.9$. The representative morphologies of ZrS_2 pillar crystals obtained are shown in **Fig. 5**. Upon increasing the gas flow ratio, plate-like crystals begin to wind to form pillar-shaped crystals (Fig. 5(a)). The side plane of the pillar crystal was usually smooth and round, but sometimes spiral and hexagonal winding steps were observed (Fig. 5(b)), suggesting the growth by the Bacon's scroll mechanism.[16]

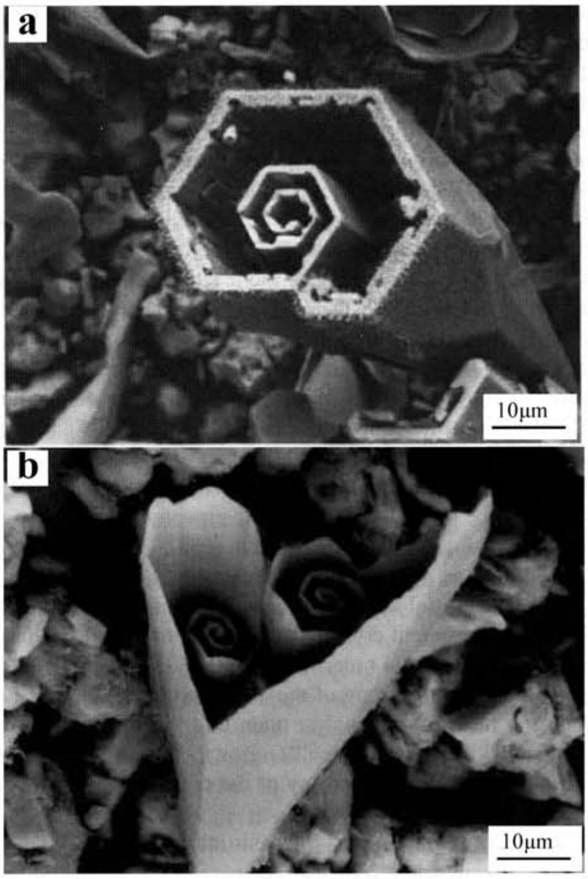

Fig. 4. (Cr, Fe)$_5$Si$_3$ spiral single crystals. (a) single-helical crystal, (b) paired-helical crystal.

2.4 Preparation of coiled ceramic fibers with 3D-helical/spiral structures by catalytic CVD process

It is well known that the presence of an impurity metal has an excellent effect on whisker growth by CVD, and frequently its role can be explained in terms of formation of a liquid phase from which whiskers grow through a vapor–liquid–solid (VLS) mechanism proposed by Wagner and Ellis.[17] Presence of some kinds of metal impurities is essential for obtaining whiskers or filamentary crystals. The kind of the most effective impurity for the crystal growth by VLS mechanism and the crystal morphology are different from compounds to compounds to be grown. Generally, Au, Pt, and Pd are widely effective for the crystal growth of various compounds

Coiled ceramic fibers (ceramic coils) with a 3D-helical/spiral structure are very interesting as new functional materials with many applications, such as light weight thermal barriers, heat exchangers, gas separation materials, absorbers for electromagnetic waves, microsensors, electrode materials, catalysts, etc. while the ceramic coils are not commercially available. The growth of various ceramic coils by catalytic CVD process has sometimes been observed with mixing straight fibers so far. However, these coiled fibers were generally very irregularly coiled, and the growth was extremely accidental and without reproducibility.

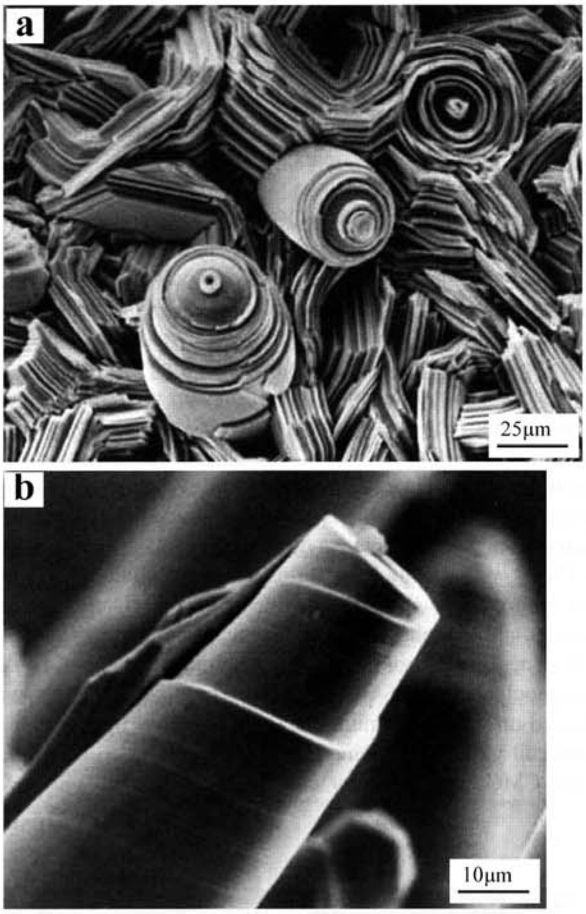

Fig. 5. (a) ZrS$_2$ spiral crystals grown among platelet crystals and (b) tip part of a pillar helical crystal.

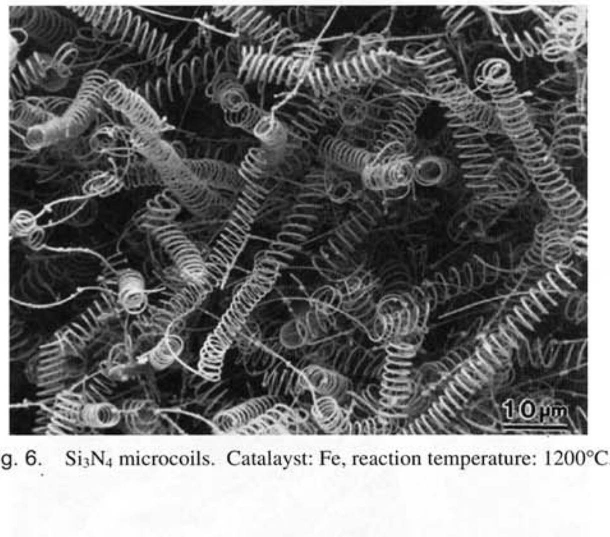

Fig. 6. Si$_3$N$_4$ microcoils. Catalayst: Fe, reaction temperature: 1200°C.

In 1989, we have first found that very regularly coiled silicone nitride fibers (Si$_3$N$_4$ microcoils) could be obtained with good reproducibility by the catalytic CVD process.[18),19)] **Figure 6** shows the representative Si$_3$N$_4$ microcoils obtained by the Fe-catalyzed CVD process using a Si$_2$Cl$_6$ + NH$_3$ (or N$_2$) + H$_2$ gas mixture at 1200°C on a graphite substrate. The Si$_3$N$_4$ coils are single-helix coils and have a coil diameter of 10–15 μm and a coil pitch of 3–5 μm. The Si$_3$N$_4$ coils have a crystalline core surrounded by an amorphous Si$_3$N$_4$ clad, and have excellent elastic and mechanical properties.

2.5 Preparation and characterization of carbon microcoils (CMC)[2)–5)]

In 1990, we have first found that carbon micro-coils (CMCs) with 3D-helical/spiral structures and coil diameters of μm orders were obtained by the metal-catalyzed pyrolysis of acetylene containing a small amount of sulfur impurities over transition metal catalysts at 700–800°C.[20] The preparation conditions, morphology, growth mechanism, microstructure and some properties of the CMCs were examined in detail.

2.5.1 Growing patterns

The carbon microcoils (CMCs) grew perpendicularly on the substrate surface with the growth tips pointing to the direction of the source gas inlets, and the thickness of coil layers reached 4–8 mm thick after 2 hrs reaction time, and the coil length reached to 5–10 mm long. The catalyst grain used was always observed on the tip part of the CMCs. The micro-coiling morphology was formed by the rotation of the catalyst grain that was exclusive growing point. The coiling (rotating) speed was about one cycle per second around the coil axis. The CMCs with various coiling morphology; regular coils, irregular coils, double coils, single coils, etc. can be obtained depending on the reaction conditions. **Figure 7** shows representative double-helix CMCs. Almost all of the CMCs were double-helix forms in which two fibers entwined with each other such as the double helix of a DNA. The coil diameter and coil pitch of these regular carbon coils have a constant value from micrometer to several hundred nanometer orders throughout a piece of carbon coils. These regular coils were obtained under the optimum reaction conditions by which maximum coil yield was obtained.

The CMCs with irregular coil diameter and coil pitch were obtained under the deviated conditions from the optimum conditions, while the coil diameters were in the range of 1–50 μm. **Figure 8** shows the irregular coils with relatively large coil diameter of ca. 40 μm. These coils have very high elasticity and extended up to 10–15 times original coil length and elastically contracted to the original coil length, and are referred to as superelastic CMCs. The number of right-clockwise coils and left-clockwise coils were about the same. The single-helix CMCs with a high purity in deposits were also obtained by the selection of the catalysts and controlling of the reaction conditions. **Figure 9** shows the representative single-helix CMCs obtained using a catalyst of Fe-38Cr-4Mn-4Mo. Their coil diameter was the similar to that of double-helix CMCs while coil pitch was as large as 1–5 μm. **Figure 10** shows an interesting morphology of a double-helix CMC which was formed from two pieces of single-helix nanocoils.

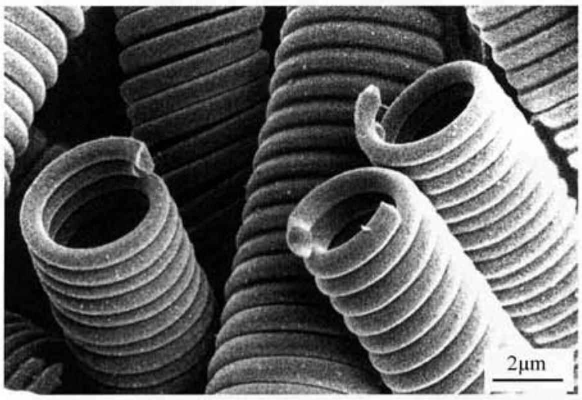

Fig. 7. Regular double-helix carbon microcoils (CMCs). Catalyst: Ni.

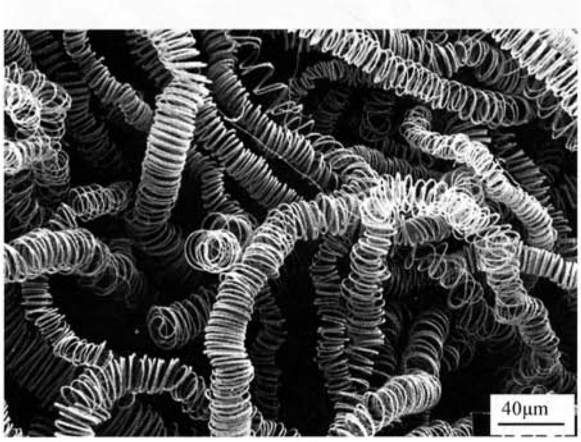

Fig. 8. Superelastic CMCs with large coil diameter. Catalyst: Ni.

2.5.2 Growth mechanism

It is very interesting to know why such a peculiar coiling morphology can be formed and what is the growth mechanism of the CMCs. A Ni single crystal plate with a (100), (111), (110) plane was used both as a catalyst and the substrate, and the effect of the respective crystal face on the coil yield was examined. It was observed that different crystal faces grew carbon coils in different coil yield, the yield order being (100) > (111) > (110). That is, there is large anisotropy of the catalytic effect of the respective crystal faces of the catalyst grain on the coil growth. From these results, we proposed the 3D-growth model of the CMCs based on the catalytic anisotropy of the crystal faces of the catalyst grain.[21),22)]

2.5.3 Composition and Microstructure

The as-grown carbon coils was 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. XRD, Raman spectra, selected area electron diffraction pattern, neutron diffraction patterns and TEM image show that the as-

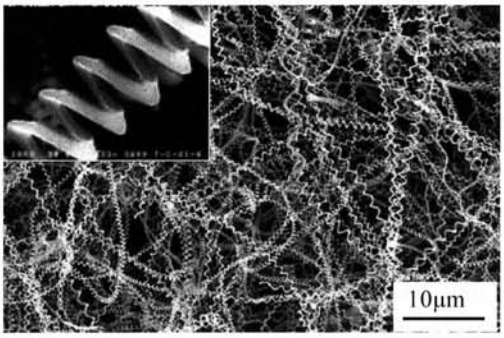

Fig. 9. Single-helix CMCs. Catalyst: Fe-38Cr-4Mn-4Mo.

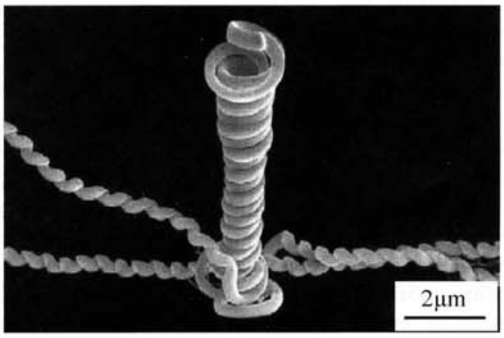

Fig. 10. Double-helix CMC grown from two single-helix nanocoils.

grown CMCs are in an amorphous state. **Figure 11** shows the schematic models of the results of neutron diffraction analysis of as grown and heat-treated CMCs. It can be seen that amorphous as-grown CMCs crystallized under high temperature heat treatments.

2.5.4 Properties

(a) Electric properties: The bulk (powder) electrical resistivity of the as-grown CMCs decreased with the increasing the bulk density, and was 1–10 Ω·cm for 0.3 g/cm^3 and 0.1–0.2 Ω·cm for 0.6 g/cm^3. The electrical resistivity of bulk CMCs increased with the increasing extension ratio, probably caused by the increase in inner stress during stretching. Electrical parameters other than resistivity; such as L (inductance), C (capacitance), Z (impedance), θ (phase angle), etc., were also changed under the extension and contraction process. The electrical conductivity of the CMCs along the helix axis was 30–50 S/cm. This conductivity is rather small with comparison to multi-wall carbon nanotubes.

(b) Electromagnetic properties:[23),24)] It is considered that the CMC is a promising candidate as a novel EM absorber, especially in the GHz range, because of its micro-coiling morphology. That is, the micro-coiling morphology is the most effective and ideal one for the generation of inductive current by Faraday's Law resulting in absorption of EM wave. Actually, the CMCs can absorb EM wave in the GHz region without reflection. For example, the reflection loss above –20dB, which corresponds to 99% absorption, was obtained for double layer of CMCs(300–500 μm)/PMMA//CMCs(150–300 μm)/PMMA at wide frequency ranges of 50–110 GHz.

(c) Mechanical properties: The circular CMCs, which is formed by the carbon fibers with circular or elliptical cross section, with a large coil diameter could be expanded up to 4.5–15 times original coil length, while flat CMCs, which is formed by the carbon fibers with flat cross section, could be expanded elastically up to only 1.5 times original length.[25)] The CMCs could be expanded linearly with the increasing in the applied load. The rupture strength of the as-grown CMCs was 42–114 MPa. The rigidity of the circular and flat as-grown CMCs were 22–46 GPa and 22–33 GPa, respectively. The CMCs was stable under mechanical stirring in water and was not ruptured.

(d) Tactile sensing properties:[26)–32)] The CMCs have a high elasticity and many electrical parameters changes by the extension and contraction. The CMCs were embedded into elastic polymers, such as polysilicone, polyurethane, elastic epoxy resin, etc. to form CMC sensor elements, and the change in electrical parameters of the elements under the application of static loads were examined, in which ac (200 kHz) voltage of 0.5 V was applied to the elements though electrodes. **Figure 12** shows the change in L (inductance) parameter of the CMC(1 wt%)/polysilicone sensor elements with a thickness 100 μm under the application of small load below 500 mgf. Apparent signal change in L parameter can be seen under the application of very small load of 1 mgf, indicated that the CMC sensor elements have a very high tactile sensitivity, which is comparable to that of human skin. We have also found that the CMC sensor elements can also detect accessing substances without touching. **Figure 13** shows the change in L parameter under accessing a hand to the

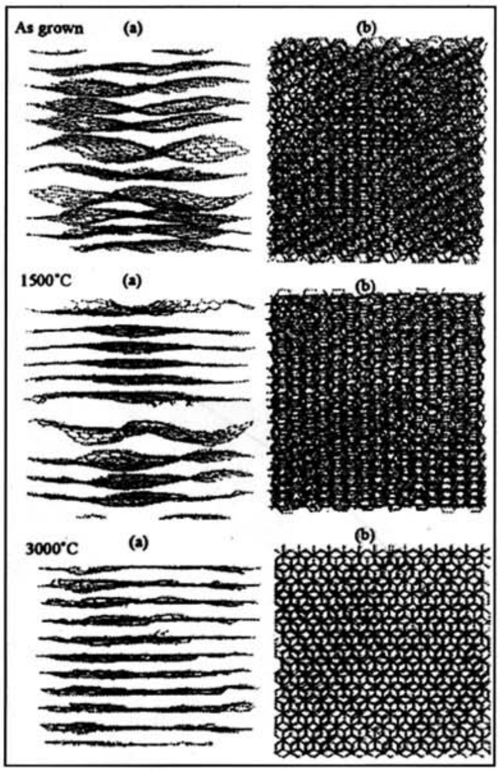

Fig. 11. Newtron diffraction analysis of as-grown and heat-treated CMCs. (a) as-grown CMCs, (b) heat-treated CMCs at 1500°C, (c) heat-treated CMCs at 3000°C.

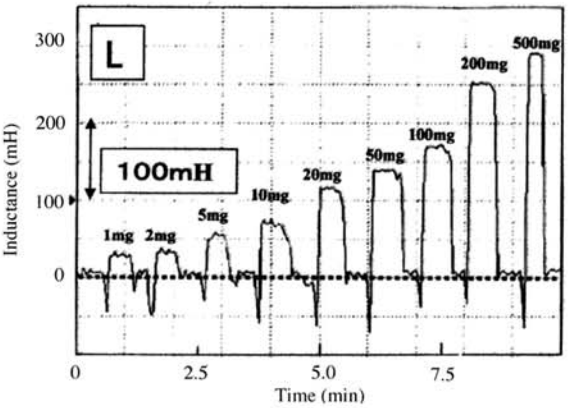

Fig. 12. The change in L (inductance) parameter of CMC/polysicilone tactile sensor elements under the application of loads.

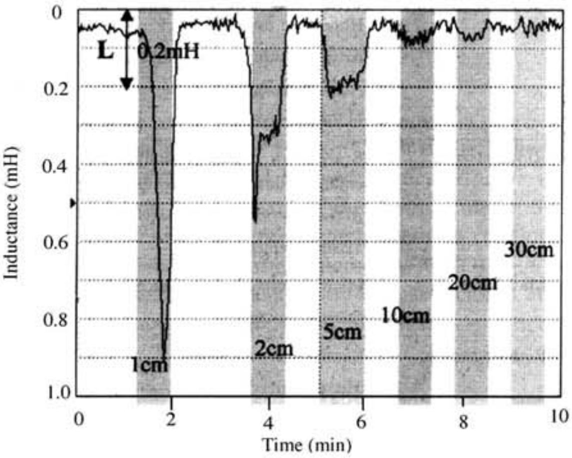

Fig. 13. The change in L (inductance) parameter of CMC/polysicilone proximity sensor elements under accessing a hand.

elements. The apparent signal change is observed at 20 mm separation and very large signal at 1 cm. These properties can be used as high sensitive tactile and nearness sensors.

(e) Breeding or anti-breeding effect on cells: Ogawa has found that the CMCs have activation effect of the breeding of the skin cell or collagens, while the reason is not yet known.[33] For example, the number of skin cell of Pam 212 increased by 1.6 times against control under the addition of CMCs by 1 μg/ml. Komura found that the CMCs has effectively generated hydroxyl radial (·OH) in aqueous solution by ultrasound exposure and are applicable to sonodynamic therapy of cancer.[34] We have found that CMCs have inhabitation effect on the breeding of keloid fibroblast, cancer cells of leukenia, or uterus.

(f) Application of CMCs:[35] The CMCs have many interesting and eminent characteristics, such as 3D-helical/spiral microstructure with μm orders in coil diameters, diverse microstructures from amorphous to graphite structure, changing in electrical parameters under the application of various stimuli, high microwave absorption and microwave heating abilities, breeding and anti-breeding effect on cells, fibrils of organisms, etc. The CMCs are now commercialized in cosmetics. The CMCs are a possible candidate for electromagnetic wave absorbers, remote heating materials, visualization elements of microwaves, tactile sensor elements, micro antenna, chiral catalysts, bio-activators or bio-deactivators, thermotherapy of cancer, energy converters, etc.

2.6 Preparation and characterization of ceramic microcoils using CMCs as a template

The carbon coils can be easily metallized and/or nitided by vapor-phase diffusion process and to form micro-coils of metal carbides and/or nitrides with a full preservation of the coiling morphology of the CMCs. Using very regular-coiled CMCs without 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) could be obtained. These modification processes are shown in **Fig. 14**. **Figure 15** shows the polished cross section of TiC/CMCs composite coils obtained by the vapor phase titanizing of CMCs templates. The white ring-like part is TiC layers and a core surrounded by the TiC layer is unreacted carbon part.[36] **Figure 16** shows TiO_2 microcoils obtained by the TiO_2 coating on the surface of single-helix CMCs templates and then heat-treated at 700°C in air.[37)–39] The resisitivity of the bulk CMCs can be decreased steeply with the surface coating by carbon, TiC, TiN, ZrC, NbC, and TaC, but not by graphitizing at high temperature heat treatment.

Table 1. Application of CMCs

1	Electromagnetic absorbers	(1) Beads
		(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.

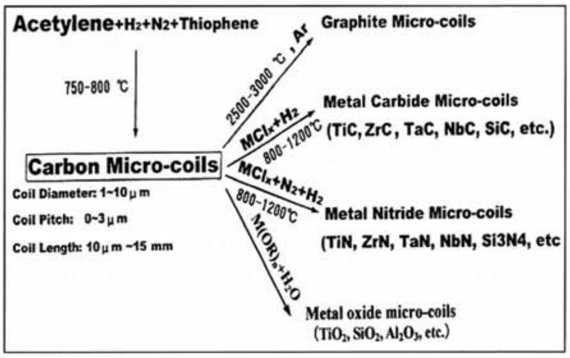

Fig. 14. Modification routes of the CMCs.

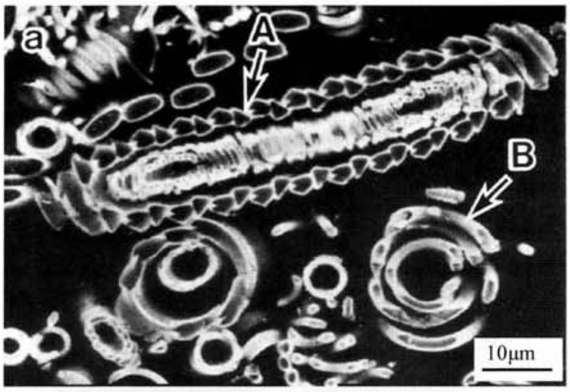

Fig. 15. Polished cross-sections of TiC/CMCs composite microcoils obtained by diffusion process of CMCs template.

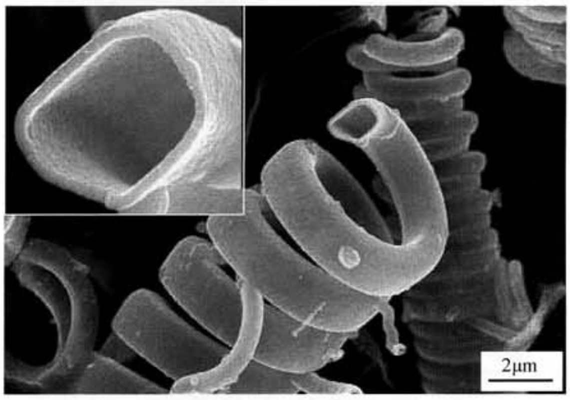

Fig. 16. TiO_2 microcoils obtained by the CVD coating of TiO_2 layers on the surface of CMCs template.

3. Conclusions

We have developed a modified hot filament method for the preparation of large bulk crystals of transition metal carbides, nitrides, silicides or borides. We have also developed a diffusion process and in-situ CVD process as modified CVD processes for obtaining single crystals with interesting morphologies of iron metal group compounds The carbon micro-coils (CMCs) with a coil diameter of μm~nm orders were first obtained by the metal-catalyzed pyrolysis of acetylene, and the preparation conditions, morphology, growth mechanism, and some properties of the CMCs were examined. The micro-coils or micro-tubes of various transition metal carbides and nitrides could be obtained by the vapor phase metalizing and/or nitriding of the CMCs with full preservation of the coiling morphology. The CMCs have many interesting and eminent characteristics, such as high elasticity, changing in electrical parameters under the application of various stimuli, high microwave absorption and microwave heating abilities, breeding and anti-breeding effect on cells, fibrils of organisms, etc. The CMCs is the most possible candidate for electromagnetic absorbers, hydrogen absorber, tactile and nearness sensor elements, tunable micro/nano devices/sensors, chiral catalysts, thermotherapy of censors, capacitors, energy converters, etc.

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