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Preparation of Ceramics/Carbon Microcoils Composites using Carbon Microcoils as a Template

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Double-helix carbon microcoils (CMC) have the special helical/spiral conformation, thus have outstanding characteristics, such as high-elasticity, electromagnetic wave absorptivity, micro-sensitivity, emittivity, etc. In this study, transferring spiral 3D-helical/spiral structures of CMC to different ceramic materials, such as TiO_2, $NiO \cdot Fe_2O_3$, SiO_2, etc., using CMC as a template was tried. Two coating processes, sol-gel and CVD processes, were used. The preparation conditions and morphologies of new ceramic microcoils/tubes were examined. Using the CVD process, different ceramic coating layers could be deposited uniformly on the outer and inner surface of CMC and well-formed ceramics/carbon(CMC)-composited coils/tubes were obtained, while by the sol-gel process it was difficult to form well-formed ceramic/carbon-composited coils/tubes.

Key words: carbon microcoil, helical ceramic microtube, template

1. INTRODUCTION

Since 1950', many researchers have been trying to prepare materials with a 3D-helical/spiral structure. Some researchers have reported the growth of coiled ceramics fibers such as carbon, SiC,[1] and Si_3N_4,[2-5] from the vapor phase. We prepared regularly micro-coiled carbon fibers (referred to as "carbon microcoils" or "CMC" hereafter) by the catalytic pyrolysis of acetylene and reported the preparation conditions, morphologies, and some properties of the products.[6-7] Materials with a microcoiled structure are potential candidates for the absorbers of electromagnetic (EM) waves, tunable micro-devices, micro-sensors, micro-actuators, activation catalysts in microorganisms, etc. We prepared various ceramic microcoils and/or microtubes, such as SiC,[8] TiC,[9] ZrC,[10] NbC,[11] TiN[12], TaN,[13] and NbN[14] by vapor phase diffusion process, with full preservation of the coiling morphology. Furthermore, we also prepared the TiO_2 microcoils and helical TiO_2 microtubes by chemical vapor deposition (CVD and sol-gel processes using CMC as the template.[15-16]

It is well known that titanium dioxide (TiO_2) with an anatase phase has notable photocatalytic activity. On the other hand, the CMC have very high absorption ability of EM waves of GHz regions.[16] It was found that EM wave absorption ability of CMC increased by coating TiO_2 layers on the CMC as well as high photocatalytic activities. Accordingly, we can expect that helical ceramics/CMC composites are potential candidates for novel phohocatalytic materials, electromagnetic (EM) absorbers, electrical microdevices, etc.

In this study, TiO_2/CMC composite microcoils/ microtubes (referred as to "TiO_2/CMC microcoils" hereafter) were obtained by coating TiO_2 layers on the CMC templates using the CVD and sol-gel processes. Furthermore, other helical ceramic coils, such as Fe_3O_4, SiO_2, Al_2O_3, were also prepared. The preparation conditions and morphologies of these helical ceramic coils were examined in detail.

2. EXPERIMENTAL

2.1 Source carbon microcoils

Carbon microcoils (CMC) used as the template were prepared by the Ni-catalyzed pyrolysis of acetylene at 770℃. A detailed preparation procedure is described in Ref. 7. The representative morphologies of the CMC are shown in Fig. 1. Very regularly-coiled CMC with a constant coil diameter of 2~10 μm and without a coil gap, as shown in Fig. 1a, were usually used as the template, and irregular coils such as shown in Fig. 1b were also used.

2.2 Metal oxide coating and calcination processes

Coating TiO_2 films on the CMC template were carried out using two processes, a sol-gel process and a CVD process. In both processes, titanium tetraisopropoxide (referred to as "TIPO" hereafter) was used as a Ti source. In the sol-gel process, ethyl alcohol solution (3ml) containing TIPO (0.2~0.8 ml) and a CMC sample (10 mg) was mixed with ethyl alcohol solution (6 ml) containing HCl (2M), stirred and dispersed by a supersonic bath, then aged (2 hr), concentrated under vacuum, dried, and heat-treated or calcinated. The concentration ratio was 25~100% (full drying). In the CVD process, the CMC template were coated with TiO_2 films using a gas mixture of TIPO+H_2O+N_2 at 300℃ for 2 hr using a rotating CVD reactor. The rotating speed was fixed at 25 rpm. The TiO_2-coated CMC sample was then heat-treated in N_2 atmosphere or calcinated in air atmosphere at 500-800℃ for 2 hr. The helical Ni-ferrite ($NiO \cdot Fe_2O_3$) -coated CMC sample was prepared by a sol-gel process using $Fe(NO_3)_3 \cdot 9H_2O$+$Ni(NO_3)_2 \cdot 6H_2O$ as the metal sources by a similar coating process as that of TiO_2. The helical SiO_2 and Al_2O_3-coated CMC were prepared by the CVD process using tetraethoxy silane (TEOS) and tetraisopropoxy aluminum were used as the metal source, respectively.

3. RESULTS AND DISCUSSION

3.1 Preparation of Helical TiO_2/CMC microcoils/tubes

Fig. 2 shows the SEM image of the TiO_2 pillar crystals obtained by the sol-gel process and calcination at 500℃ in air, in which the addition amount of TIPO was 0.2 ml. The CMC template was burned out during the calcination process and the residues (deposits) were TiO_2 polycrystals. Fig. 2a shows pillar-like TiO_2 deposits with large crack along the pillar axis. Large pores are also sometimes observed in the pillar deposits as shown in Fig. 2b. These pillar TiO_2 deposits were formed by the calcinations of TIPO impregnated by the capillary phenomenon into a core tube present along the coil axis of the regular CMC. Crack or large pore is formed by the contraction of the deposits. Fine TiO_2 grains were deposited densely in the pillar deposits as can be seen in the vertical ruptured cross section. Regular and negative coiling patterns are observed on the surface of the pillar deposits, and curved inner smooth surface (arrow A) was of the TiO_2 layers deposited on the inner surface of the core pore (pipe) of the CMC template. That is, negative coiling patterns observed on the surface of pillar TiO_2 deposits are transcipted patterns of the inner surface of the pore (pipe) present along the coil axis of regular CMC template. Increasing the TIPO addition amount (0.4 ml), thin outer TiO_2 coils were also observed on the outer surface of inner pillar TiO_2 deposits as shown in Fig. 3. Further increasing the TIPO addition amounts (0.8 ml) resulted in the formation of only outer TiO_2 thin coils and inner pillar TiO_2 deposits were not observed as shown in Fig. 4. These TiO_2 thin coils were obtained by the collection of thick TIPO solution layer on a channel between two adjacent fibers from which the CMC template was constructed. These phenomena was considered to be affected by the of solution, and a formation model of TiO_2 by sol-gel process was reported.[16] Using the CVD process, more uniform TiO_2 layers with smooth and uinform thickness than that using the sol-gel process were obtained.[16] The thickness of TiO_2 layers increased with increasing the gas flow rate of TIPO.[17] We have reported that the optimum gas flow rates of TIPO and H_2O for obtaining the TiO_2-coated CMC with uniform TiO_2 layers and high yield

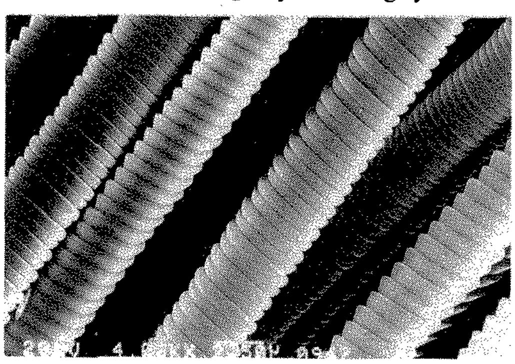

Fig. 1. Representative carbon microcois (CMC) used as the template.

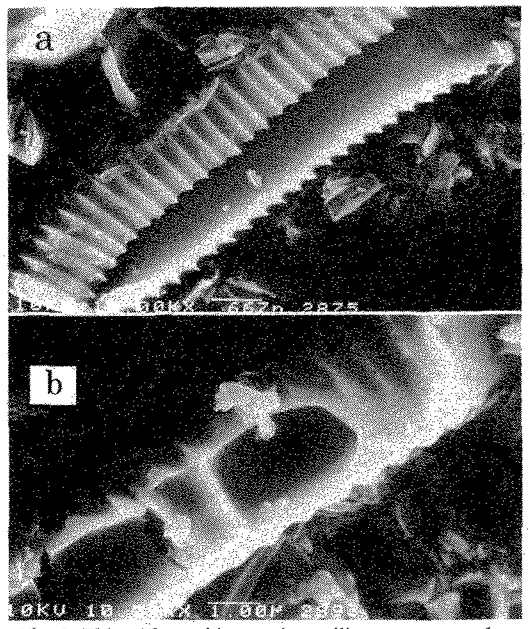

Fig. 2. TiO_2 pillars with negative coiling patterns on the surface. (sol-gel process, TIPO: 0.2 ml)

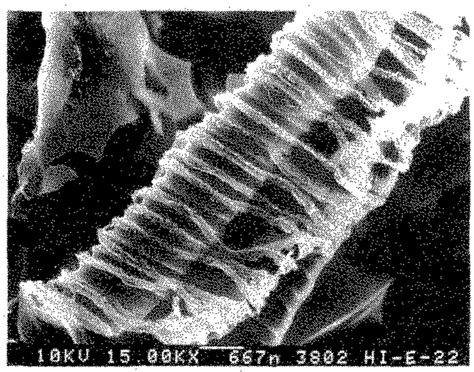

Fig. 3. Outer Thin TiO_2 microcoils and inner TiO_2 pillars. (sol-gel process, TIPO: 0.4 ml)

were 6.4 ml/s and H_2O=13.9 ml/min respectively.[16] Fig. 5 shows the effect of total gas flow rate of N_2 on the thickness and weight increase of TiO_2, in which TIPO and H_2O gas flow rates were fixed at 6.4 ml/min and 13.9 ml/min, respectively. The thickness and weigh gain of TiO_2 decreased with increasing N_2 flow rate. By the N_2 flow rate below 1100 ml/min, powder-like TiO_2 grains without adherence were deposited on the surface of CMC. On the other hand, discontinuous thin TiO_2 films were deposited. The optimum N_2 flow rate for obtaining uniform and thick TiO_2 layers was about 1600 ml/min. Fig. 6 shows the surface appearance CMC coated with TiO_2 layers.

Fig. 7 shows the ruptured cross section of the helical TiO_2 microtubes with an uniform TiO_2 thickness. Fig. 8 shows the XRD patterns of the helical TiO_2 microtubes. It can be seen that the main peaks is anatase TiO_2 phase and no peaks of rutile were observed. The lattice constants of the helical TiO_2 microtubes was a=0.379nm and c=0.979nm, in accordance with that of anatase TiO_2

phase. The specific surface area of the helical TiO_2 microtubes was 1.4 m^2/g while source CMCs was about 100 m^2/g, indicating having very dense structure.

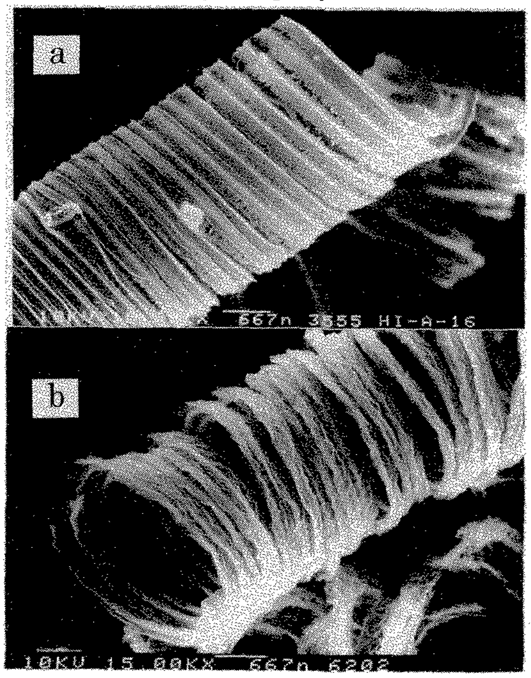

Fig. 4. Helical TiO_2 microocils. (sol-gel process, TIPO=0.8 ml)

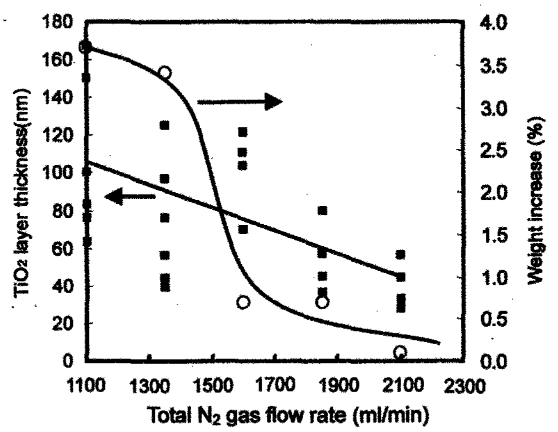

Fig. 5. Effect of totoal N_2 flow rate on the thickness and weigh increase of TiO_2. TIPO gas flow rate: 6.4 ml, H_2O gas flow rate:13.9 ml.

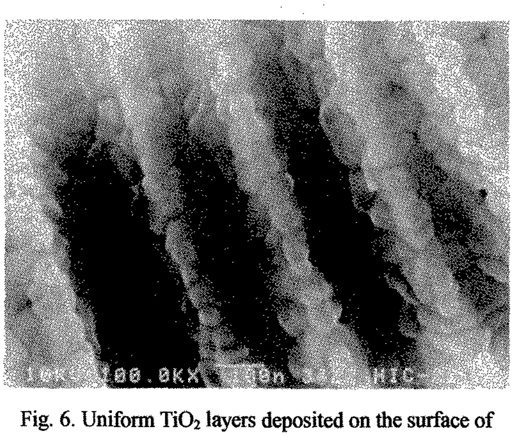

Fig. 6. Uniform TiO_2 layers deposited on the surface of on the CMC. (CMC process)

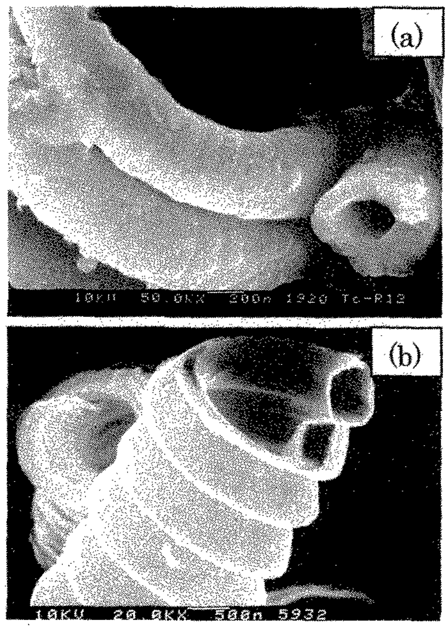

Fig. 7. Helical TiO_2 microocils.
(CVD process, N_2 flow rate: 1600 ml/min)

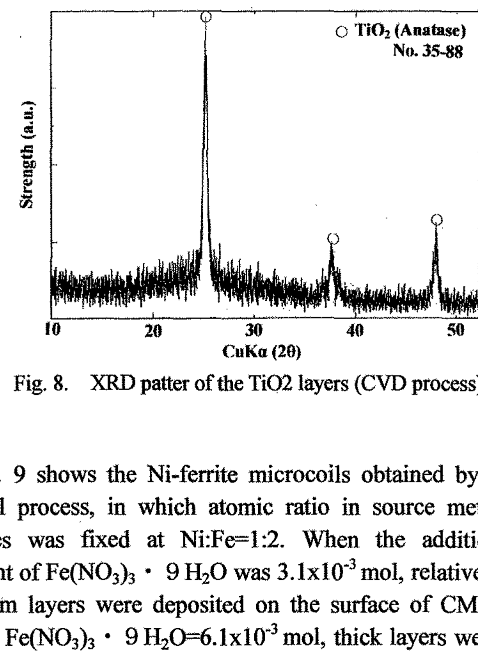

Fig. 8. XRD patter of the TiO2 layers (CVD process)

Fig. 9 shows the Ni-ferrite microcoils obtained by a sol-gel process, in which atomic ratio in source metal nitrates was fixed at Ni:Fe=1:2. When the addition amount of $Fe(NO_3)_3 \cdot 9H_2O$ was 3.1×10^{-3} mol, relatively uniform layers were deposited on the surface of CMC. Using $Fe(NO_3)_3 \cdot 9H_2O = 6.1 \times 10^{-3}$ mol, thick layers were deposited and some cracks and the exfoliation of the TiO_2 layers were observed. XRD patterns (Fig. 10) showed that the obtained layers was a trevorite nickel ferrite ($NiO \cdot Fe_2O_3$) phase.

The helical SiO_2 or Al_2O_3 microcoils were also easily obtained by the CVD process under the similar preparation conditions as that of TiO_2 coils.

4. CONCLUSIONS

Helical TiO_2/carbonmicrocoil(CMC) microcoils/ microtubes were obtained by the sol-gel and chemical vapor deposition (CVD) processes, in which titanium tetra-isopropoxide was used as a Ti source. The preparation conditions and morphologies were examined in detail. Using a sol-gel process, thin helical TiO_2 microcoils templated the grooves between adjacent two coils or helical TiO_2 pillars with coiling patterns on the outer surface were obtained depending on the coating conditions. On the other hand, using a

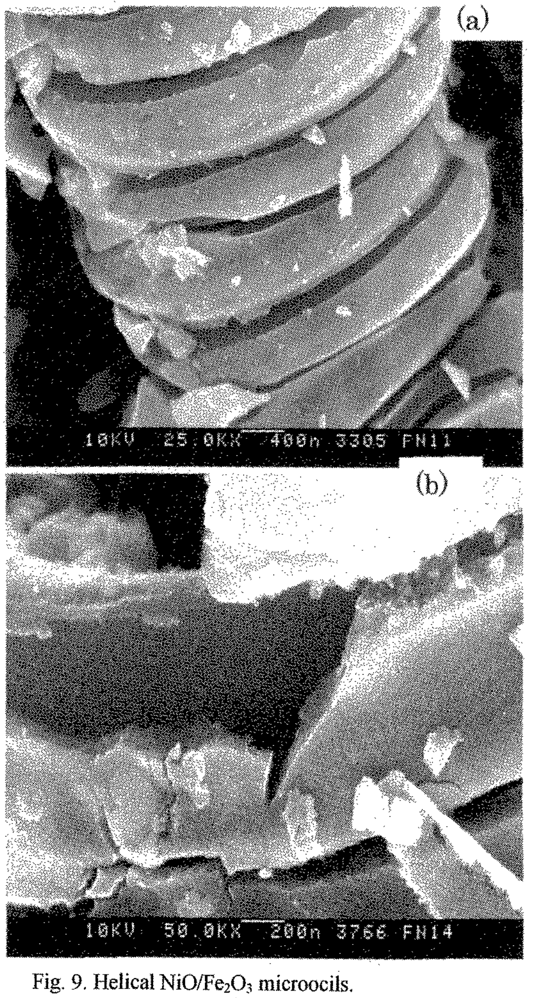

Fig. 9. Helical NiO/Fe_2O_3 microocils.
(a) $Ni(NO_3)_2 \cdot 6H_2O$: $1.61x10^{-3}$ ml, $Fe(NO_3)_3 \cdot 8H_2O=3.1x10^{-3}$ mol, (b) (a) $Ni(NO_3)_2 \cdot 6H_2O$: $3.1x10^{-3}$ ml, $Fe(NO_3)_3 \cdot 8H_2O=6.1x10^{-3}$ mol.

CVD process, helical TiO_2/CMC with uniform TiO_2 thickness were obtained. The optimum gas flow rates for obtaining the TiO_2-coated CMC with uniform TiO_2 layers and high yield were as follows; TIPO=6.4 ml/s, H_2O=13.9 ml/min, and total gas flow rate=1600 ml/min. Helical $NiO \cdot Fe_2O_3$, SiO_2 and Al_2O_3 coils were also easily obtained using a sol-gel or CVD processes.

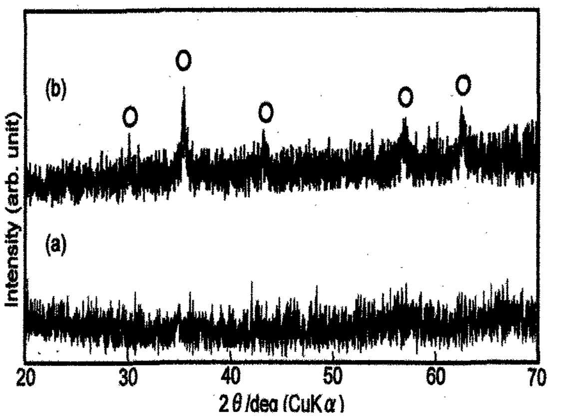

Fig. 10. XRD pattern of Ni-ferrite deposits. (sol-gel process)

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