JOURNAL OF MATERIALS SCIENCE **39** (2004) 2727–2736

Vapor-phase formation of single-helix carbon microcoils by using WS_2 catalyst and the morphologies

S. YANG, X. CHEN, S. MOTOJIMA
Department of Applied Chemistry, Faculty of Engineering, Gifu University, Gifu 501-1193, Japan
E-mail: motojima@apchem.gifu-u.ac.jp

Very regular single-helix carbon microcoils of outer coil diameter 1–3 μm, inner coil diameter 0.5–2 μm, and coil pitch 1–2 μm were prepared by the WS_2-catalyzed pyrolysis of acetylene in the presence of thiophene impurity. The effects of reaction temperature and thiophene gas flow rate on the growth of single-helix carbon microcoils and the morphology were examined in detail. The optimum reaction temperature was 780°C, and optimum gas flow rate of thiophene, acetylene, hydrogen and argon for obtaining regular single-helix carbon coils with a constant coil diameter were 0.2, 40, 90, and 30 sccm, respectively. The formation mechanism of the single-helix carbon microcoils is discussed.

1. Introduction

In 1953, Davis and coworkers were the first to report the vapor growth of thin carbon fibers twisted with each other in the form of a rope [1, 2]. The observation of helical/spiral-coiled carbon nanofibers, with a fiber diameter of several tens to several hundred nanometers and coil diameter of several micrometers to several nanometers by using a CVD process, were then reported occasionally by some carbon filament researchers. For example, from 1970 to 1980, Baker and coworkers reported the observation of twisted-carbon fibers among the straight carbon filaments obtained by using Fe-group catalyst [3–5]. Furthermore, they extensively studied the effects of Fe, Cu, Pt, Sn and other metal oxide catalysts on the growth of carbon filaments and observed sometimes the growth of helical/spiral-formed carbon fibers. Boehm also observed the growth of braided carbon fibers from vapor phase [6]. However, the helical/spiral-formed carbon fibers grown by the CVD process was extremely accidental and the reproducibility was very poor. There has not been researchers focused on the preparation of carbon microcoils until we found that regularly microcoiled carbon fibers (abbreviated to as "CMCs" hereafter) with double helix and chiral conformation could be obtained by the Ni-catalyzed pyrolysis of acetylene containing a small amount of sulfur or phosphorus impurity, and also reported the morphologies, growth mechanism and some properties of the products since 1990 [7–16]. Besides Ni powders or plates as the catalyst, we also investigated the preparation of CMCs by using various powders or plates of other transition metals such as Co, Cr, Fe, Hf, Mn, Mo, Nb, Ta, Ti, V, and W [7–9] and metal carbides as well as MoS_2 [11] as the catalyst. Except for Fe, all these catalysts were proved to be able to obtain more or less CMCs, but the yields were lower than using Ni. It was observed that hydrogen and a small amount of sulfur/phosphorous-containing compounds were indispensable for the growth of regular CMCs with a constant coil diameter and coil pitch in high coil yield. However, in the case of MoS_2, CMCs can be obtained without the addition of thiophene. So far, there has not been any report on the growth of CMCs over WS_2 catalyst.

Vapor grown CMCs take a special 3D-helical/spiral morphology, which is the fundamental structure of all objects, and their growth mechanism is very interesting theoretically. Because of the intriguing micro-spring and chiral conformation as well as the 3D-helical/spiral

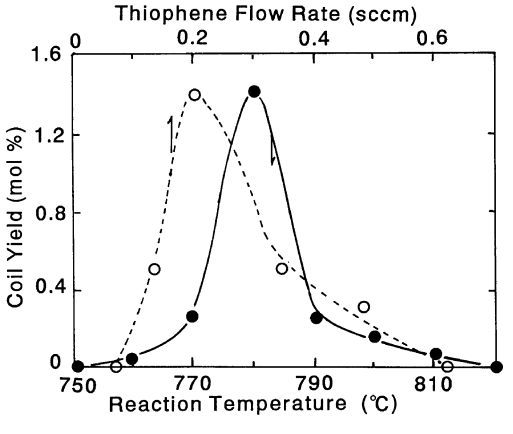


Figure 1 Effect of the reaction temperature and thiophene gas flow rate on the coil yield. (●) Thiophene gas flow rate: 0.3 sccm, (○) reaction temperature: 780°C.

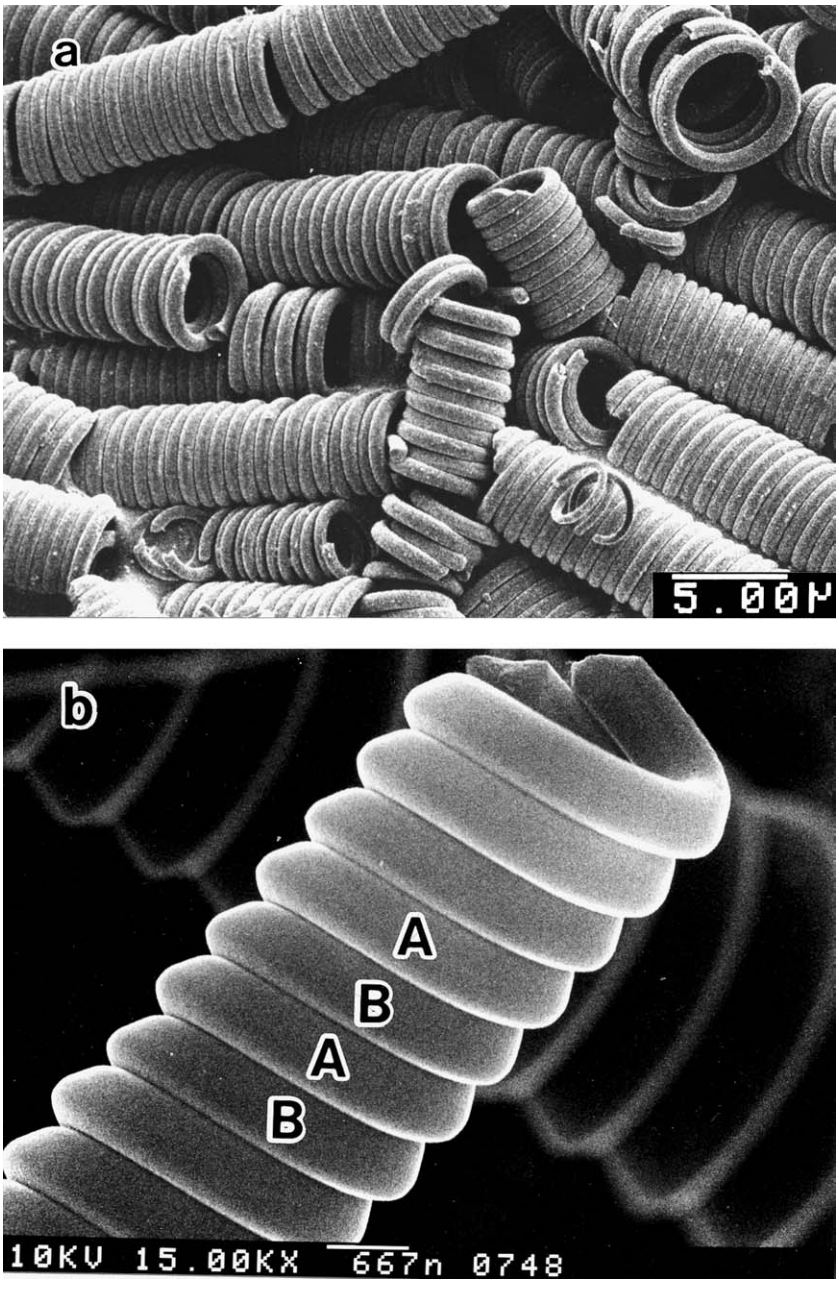


Figure 2 Representative double-helix carbon microcoils obtained by using Ni catalyst. A and B indicates different coils.

structure of the CMCs, they have many unique characteristics, such as good chiral conductivity, high surface area [15], and very high super-elastic property [16]. These unique and marvelous combination of properties makes the CMCs a very attractive material for micro/nanosensors and actuators, such as micro-magnetic sensors [17], electromagnetic wave absorbers [18–20], mechanical microsprings or actuators [21], high elastic nano-electric conductors, etc. and thus have many potential applications. These excellent characteristics are mainly affected by the special chiral/coiling morphology and the dimensions. Therefore, the development of the controlling process of the special chiral/coiling morphology and dimension, and also the effective production process of the CMCs are very important.

In this study, we prepared the single-helix CMCs by the WS_2-catalytic pyrolysis of acetylene containing a small amount of thiophene. We examined the coiling patterns, morphologies, and microstructure of the obtained CMCs in detail and also proposed the growth mechanism. It was observed that by using WS_2 as the catalyst, single-helix CMCs with a constant coil diameter of submicrons and large coil pitch could be obtained.

2. Experiment

The vertical reaction tube (quartz, 600 mm length, 40 mm i.d.) was heated from the outside by nichrome elements. The graphite plate, on which the WS_2 powder catalyst (5 μm) was dispensed, was used as the substrate, and was set on the central part of the reaction tube. A gas mixture of acetylene, thiophene, hydrogen and argon was introduced into the reaction tube through the upper gas inlets. The flow rate of acetylene, hydrogen and argon were set in 40, 90 and 30 sccm, respectively. For the reference catalysts, Ni and W metal powders was also used as the catalyst for comparing the preparation conditions and morphology of the grown

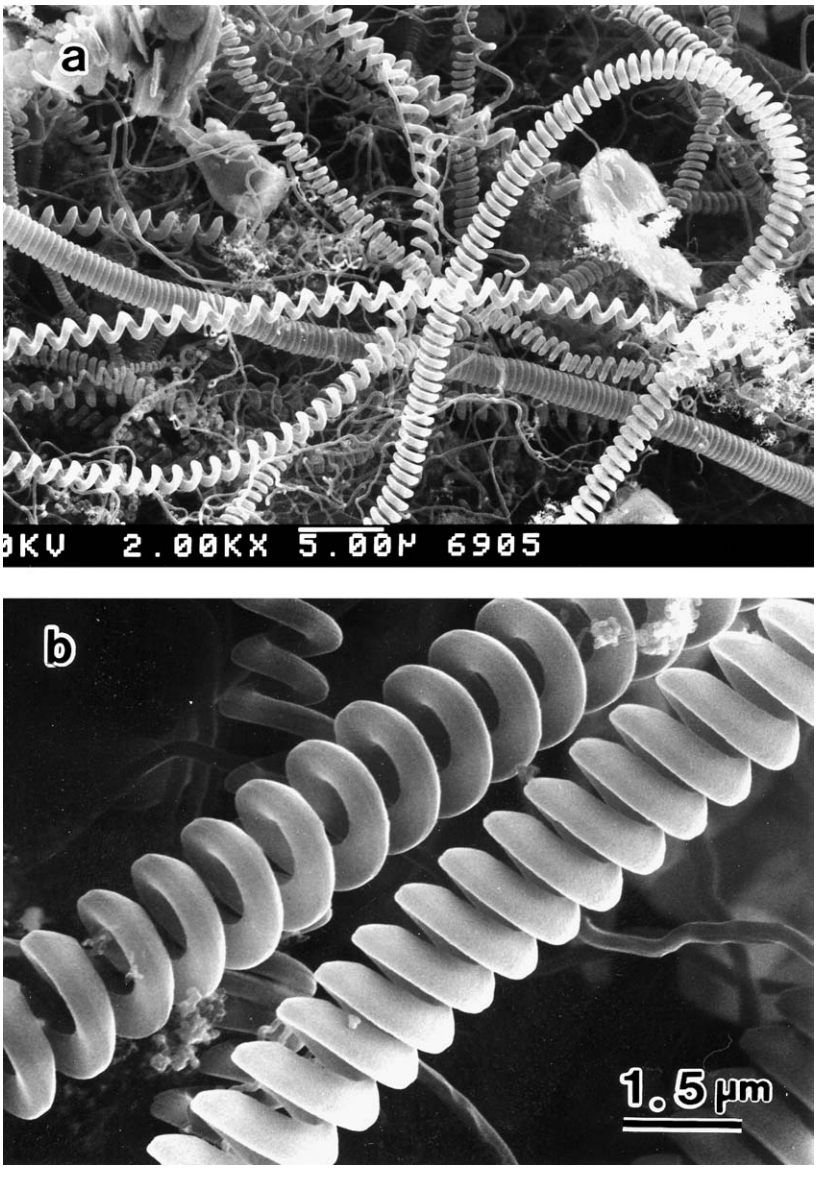


Figure 3 (a) Representative single-helix carbon coils obtained by using WS_2 catalyst and (b) the enlarged view.

coils. The schematic diagram of experimental apparatus can be cited in Ref. 8.

3. Results and discussion

3.1. Preparation conditions

The CMCs grew on the substrate surface as blanket-like appearance. The effects of reaction temperature and gas flow rate of the thiophene impurity on the coil yield are shown in Fig. 1, in which the coil yield was estimated from the ratio of the obtained CMCs against introduced acetylene. It can be seen that the coil yield was significantly affected by the reaction temperature and the optimum reaction temperature, at which the maximum coil yield was obtained, for the growth of the CMCs was about 780°C. When the reaction temperature was lower than 760°C or higher than 800°C, almost no carbon coils grew. Hereafter the reaction temperature was fixed at about 780°C. Without the addition of thiophene as an impurity, only carbon powder deposited, probably caused by higher thermal decomposition rate of acetylene without the poisoning effect by sulfur. The coil yield increased sharply with increasing thiophene gas flow rate, and attained a maximum coil yield of 1.4 mol% at the flow rate of about 0.2 sccm (about 0.13 mol% in total gas flow), and then steeply decreased with a further increase in the flow rate. At this optimum thiophene gas flow rate, regular and long single-helix CMCs, as will be shown later, grew on the substrate surface. That is, single-helix CMCs can be obtained in the maximum coil yield of about 1.4 mol% against introduced acetylene when reaction temperature and thiophene gas flow rate are the most suitable values.

3.2. General morphologies of double-helix carbon coils prepared by conventional Ni catalyst

When using a conventional Ni powder as the catalyst, under the reaction temperature range of 760–790°C, acetylene gas flow rate of 30–50 sccm, thiophene gas content in total gas flow of 0.6–0.8 mol%, and gas flow ratio (H_2/C_2H_2) of 3–4, regular CMCs without coil gap

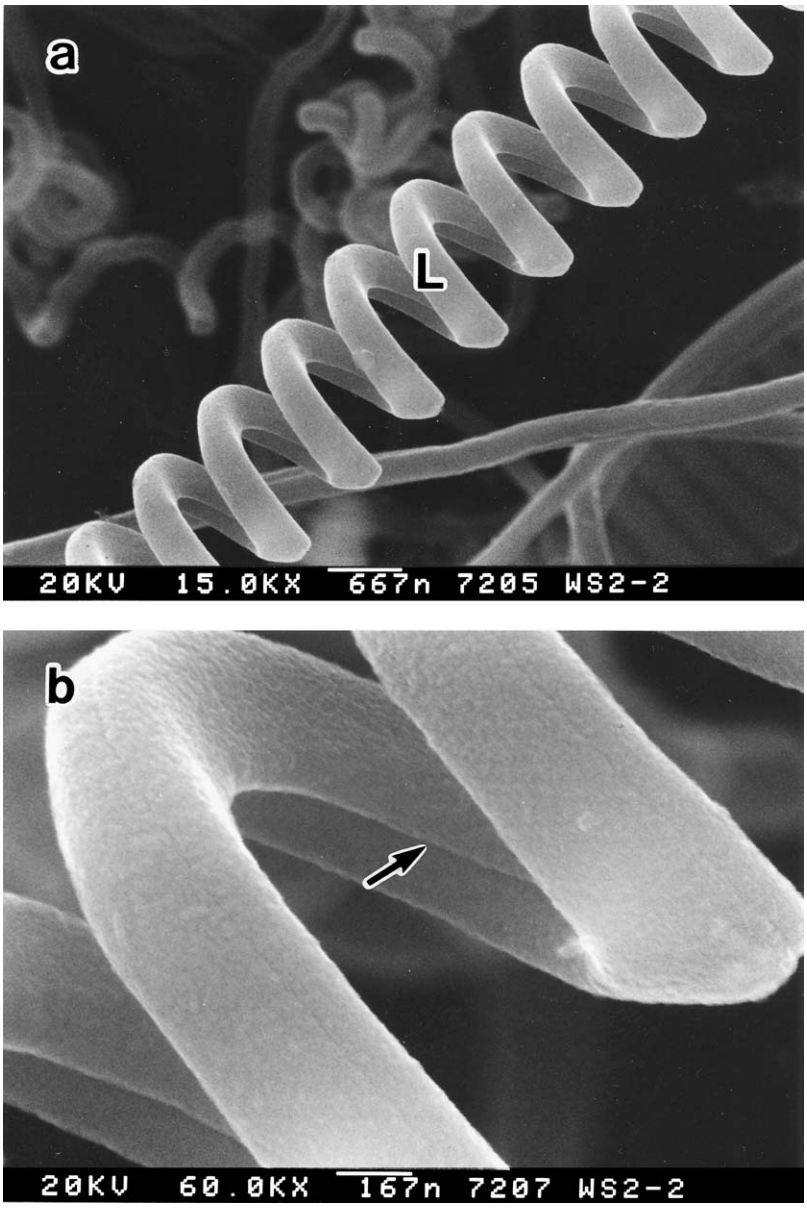


Figure 4 (a) Left-clockwise coiled single-helix carbon coil and (b) the enlarged view. Arrow in (b) indicates a deep gutter.

grew perpendicularly on the graphite substrate pointing in the direction of the source gas inlets and the high coil yield as high as 10–15 mol% was obtained [15]. Using W metal powder as the catalyst, with the same reaction condition as that using Ni or WS_2 catalyst, double helix carbon coils which have same morphology with those grown over Ni powder were generally obtained [22].

3.3. Morphologies of regular single-helix CMCs prepared by WS_2 catalyst

The CMCs, which were obtained by using a conventional Ni or MoS_2 catalyst, were usually double-helix coiled forms, in which two fibers entwined with each other such as the double-helix of a DNA, and generally with fiber diameter 0.5–0.8 μm, coil gap zero, outer coil diameter 3–7 μm, inner coil diameter 2–6 μm, and coil length 1–10 mm as shown in Fig. 2. The CMCs with coiling-chirality of right-clockwise (*R*) and left-clockwise (*L*) coiling directions were observed and the numbers of the *R* and *L* were almost the same.

We found that the coiling morphology of the CMCs obtained by using WS_2 catalyst were different from those prepared over the Ni or MoS_2 catalyst. Fig. 3 shows representative SEM images of the CMCs obtained by using the WS_2 catalyst. The CMCs obtained by using WS_2 catalyst was generally regular single coil, which was formed from a piece of carbon fiber and coil, with an outer coil diameter 1–6 μm, inner coil diameter 0.5–2 μm, coil gap 0–2 μm, and the coil length 0.5–1mm. The coiling direction of the single coil was either right-clockwise (*R*) or left-clockwise (*L*) directions and the numbers of the *R* and *L* were almost same as that of the double-helix CMCs obtained by using Ni or MoS_2 catalyst. Fig. 4 shows the left-clockwise single coil. It can be seen that a deep gutter is formed in an inner side of the coil. These gutters also observed on the right-clockwise single coil as shown in Fig. 5. Furthermore shallow striation can be seen on the outer surface of the coils (arrow in Fig 5c). Fig. 6 shows the ruptured part of a single coil. It can be seen that an apparent gutter (arrowed) exists on the outer surface of the coil, and

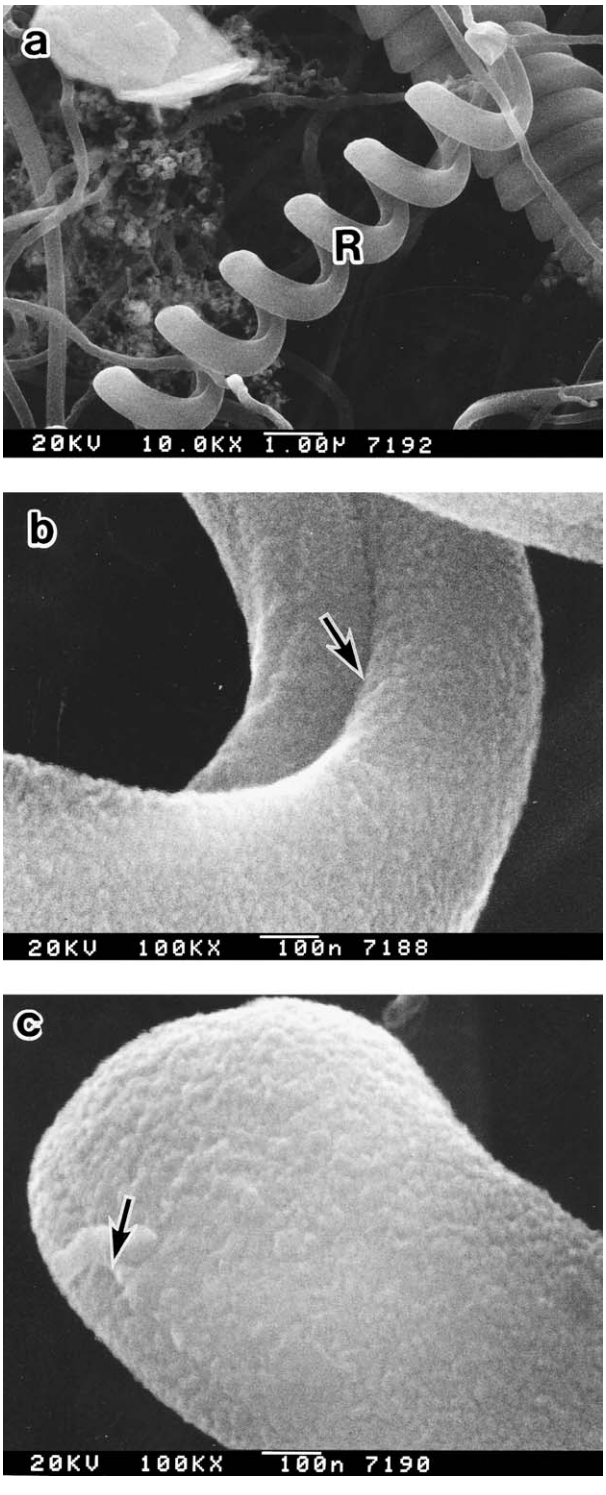


Figure 5 (a) Right-clockwise coiled single-helix carbon coil and (b and c) the enlarged view. Arrow shown in (b) indicates a deep gutter observed in the inner part of the coil, Arrow in (c) indicates a striation observed on the outer part.

that the single coil is composed of two parts (A and B). Fig. 7 also shows the ruptured cross section of the single coil. These results suggest that the carbon fiber and coil is composed by two pieces of a carbon fiber and a coil.

Sometimes, the CMCs with densely coiled tube-like forms (arrow) grew among the single-helix CMCs with different coil gaps as shown in Fig. 8. It can be seen from Fig. 8b that the tube-like coil is a single coil with the outer coil diameter of 2 μm and inner pore diameter of 1 μm. The densely coiled tube-like single coil is also considered to be formed from two pieces of a carbon fiber in which two fibers are densely coalesced with each other to form a single fiber, as can be seen in the ruptured cross section of Fig. 9. Fig. 10 shows another type of the densely coiled CMCs in which the coil composed of two coils with smaller coil diameter (*A*) and larger coil diameter (*B*).

Using the WS_2 catalyst, the growth of coiled or twisted ribbon-like carbon fibers with a fiber width of 5–6 μm, thickness of 0.5–1.5 μm and twisting gap of 10–15 μm were also sometimes observed among the single coils as shown in Fig. 11, while the growth of these ribbon-like coils was rarely observed using Ni or MoS_2 catalyst.

These observations of morphology indicate that the conformation of the single-helix CMCs is quite different from double-helix CMCs obtained by using Ni or MoS_2 catalyst and suggest a different growth mechanism.

3.4. Growth mechanism

Using the Ni catalyst, a fine Ni catalyst grain with cubic form, from which two carbon fibers grew to the opposite direction and curling and then entwining each other to form double-helix CMCs, was always observed on a tip of the CMCs. It is considered that the driving force of the formation of double helix CMCs is the anisotropic properties between three or four crystal faces of Ni_3C catalyst grain [23–25]. On the other hand, using the WS_2 catalyst, a catalyst grain as shown by arrow in Fig. 11a and in the enlarged view in Fig. 12, from which only a piece of CMCs grew, was observed on the tip of the single-helix CMCs as shown in Fig. 12. The WS_2 has a layer structure of C7 type and shows preferential crystal faces of (000n), and thus have large anisotropic properties between respective crystal faces. Based on the above observation, we proposed the growth model of the single-helix CMCs from the WS_2 catalyst as shown in Fig. 13. On the front surface of the WS_2 catalyst grain as shown by C face in Fig. 13, acetylene is decomposed to from tungsten carbide phases and this tungsten carbides diffuse to the two rear faces (A and B) and decompose to form fine carbon grains and grow into a carbon fiber. The presence of W, C, S and O was identified by electron probe microanalysis on the surface of the catalyst grain. Accordingly, thin layer composed of W-C-S-O quadruple elements may be formed on the surface of the catalyst grain as in the case of Ni catalyst [24, 25]. The anisotropy of the carbon deposition on the respective crystal faces of the catalyst grain may be caused by the different contents of elements on the respective crystal faces. Without addition of thiophene in the reaction atmosphere, no carbon coil was obtained, probably caused by the decrease of sulfur component from the thin surface layers, as a result of the decomposition of W-C-S-O and vaporization of sulfur, or inclusion of sulfur into the carbon fibers. Because of large anisotropic properties of the WS_2 crystals, once one fiber grew from the catalyst grain, the growth of another fiber may be suppressed, thus formed a single coil. The particle diameter of the WS_2 powder catalyst is several microns, but the grain size observed in the

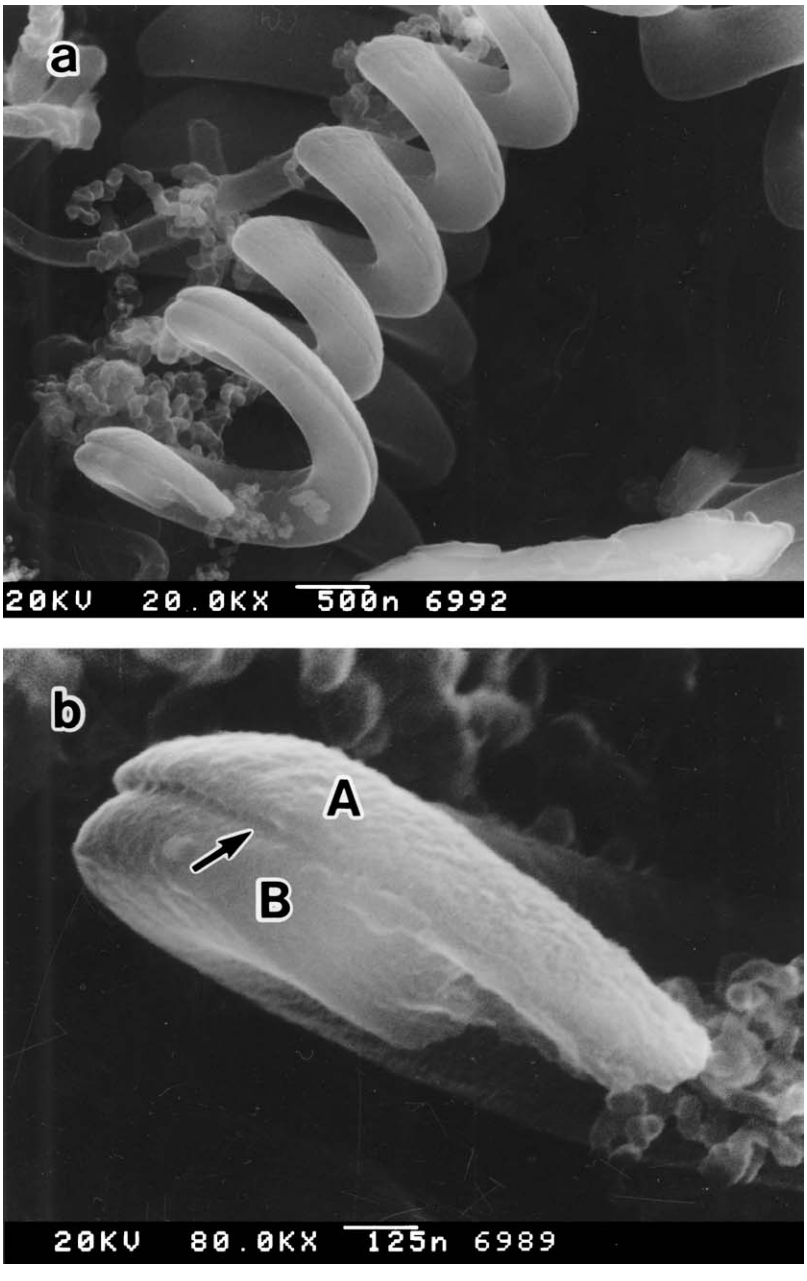


Figure 6 Ruptured cross-section of a single-helix carbon coil (1). A and B shown in (b) indicates different part of the coil, and arrow is a striation.

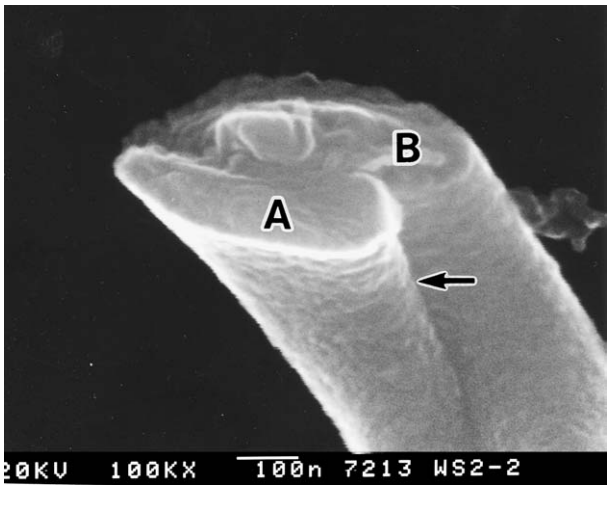


Figure 7 Ruptured cross section of a single-helix carbon coil (2).

growth tip is several hundred nm. It is well known that the form and size of the catalyst particle is ultimately responsible for determining the diameter of the grown carbon fibers. That is, the active catalyst grain actually used for the growth of carbon coils was considerably smaller than those of the source (starting) catalyst metal powders, suggesting the fragmentation of the starting catalyst grain occurred prior to the growth of the carbon fibers.

Variations in the chemical nature of the gas environment can have a dramatic influence on the prevailing crystallographic characteristics of the catalyst particles. It has been shown that the introduction of controlled amounts of sulfur in the reaction atmosphere promotes the reconstruction of the metal catalyst surface and enhances the catalytic conversion of hydrocarbons toward the formation of carbon nanostructure [26, 27]. The coil

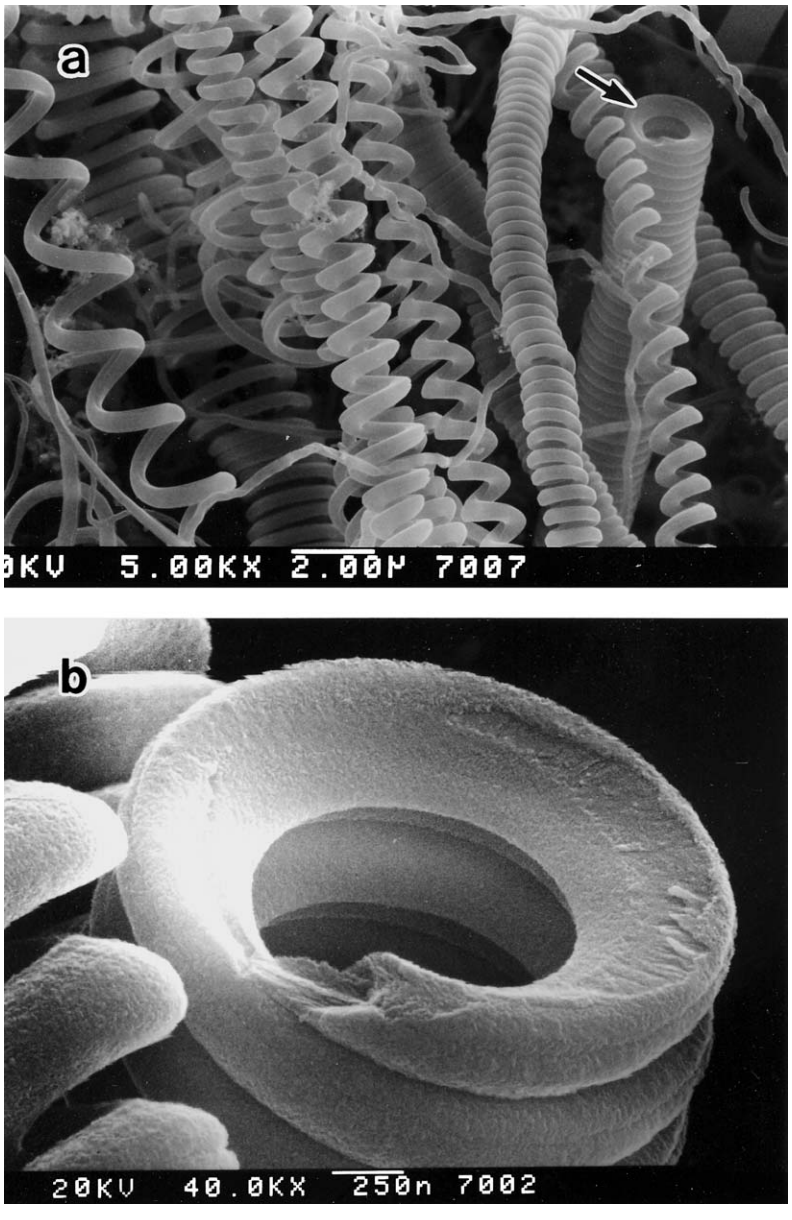


Figure 8 (a) Densely-coiled tube-like carbon coil (arrow) and the enlarged view.

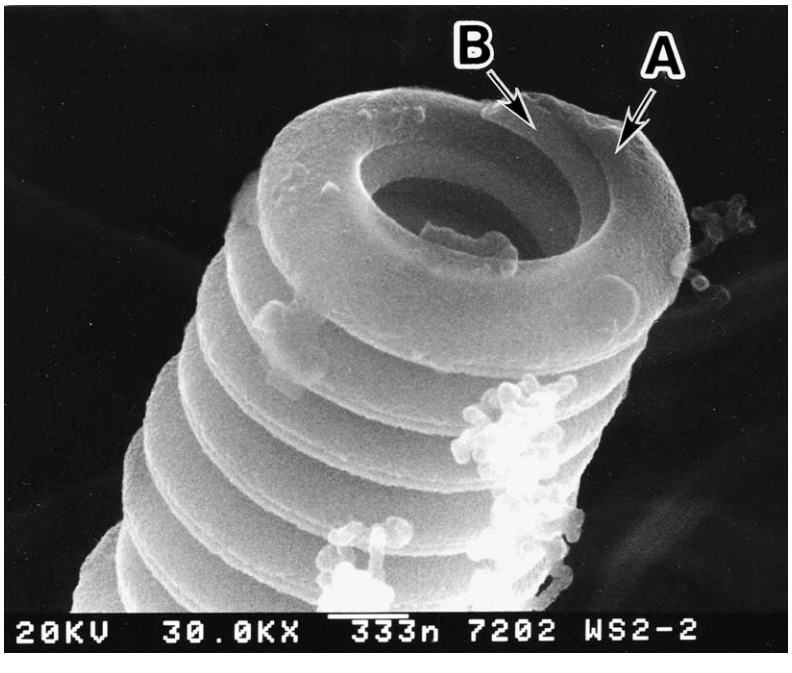


Figure 9 Densely-coiled tube-like carbon coil. A and B indicates different part of the coil.

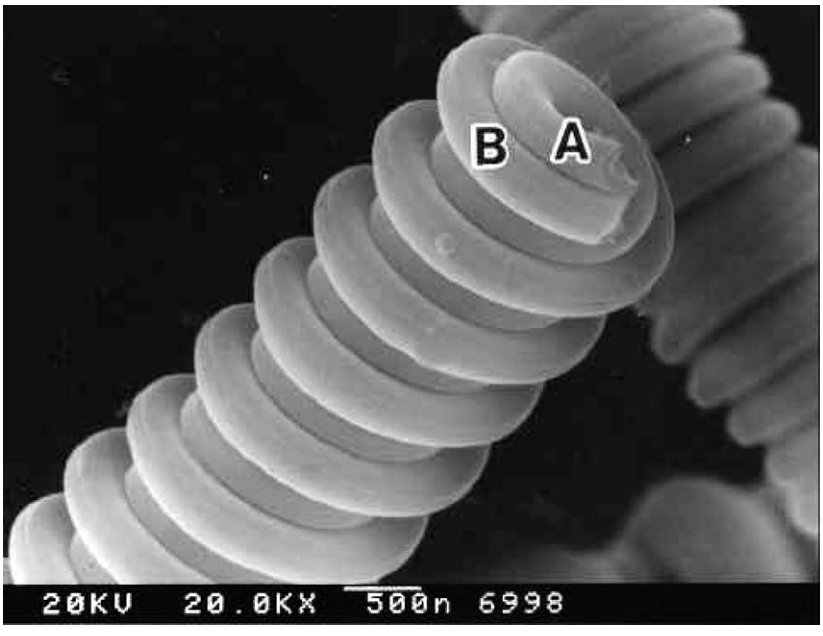
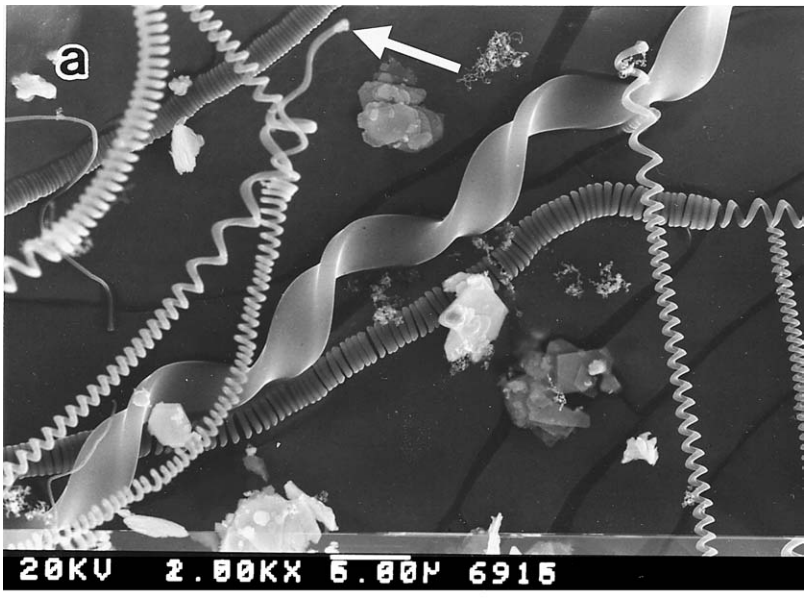


Figure 10 Double-helix coils with different coil diameter. A and B indicates different coils.



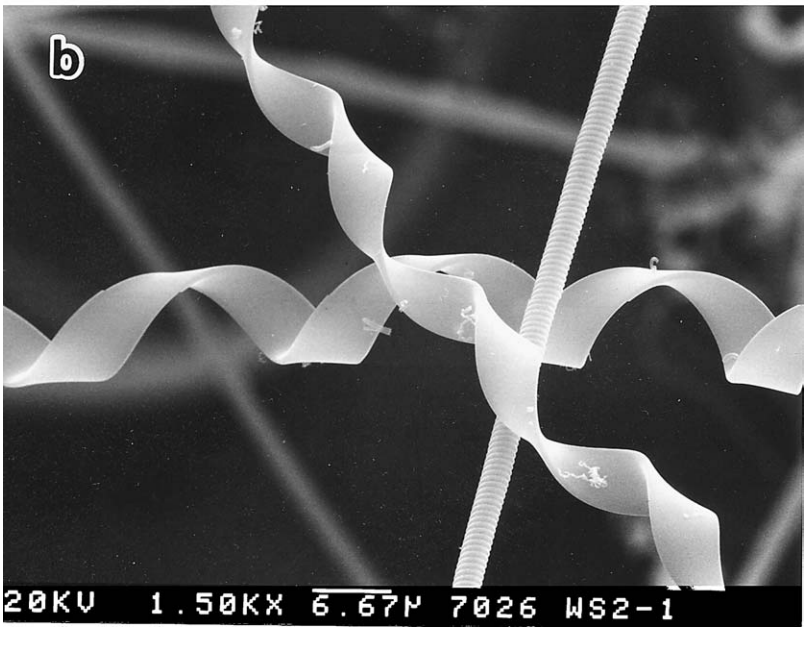


Figure 11 Helically-coiled or twisted ribbon-like carbon fibers.

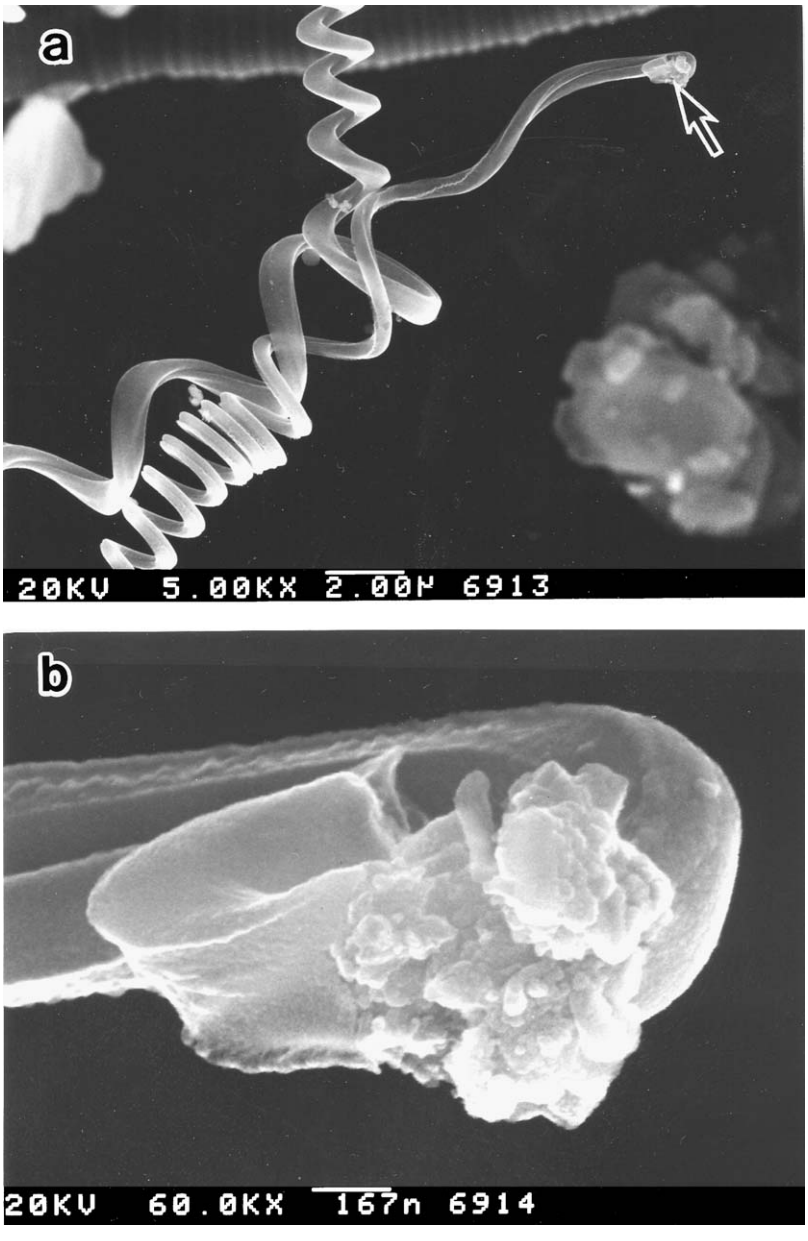


Figure 12 (a) Tip part of s single-helix carbon coil and (b) the enlarged view.

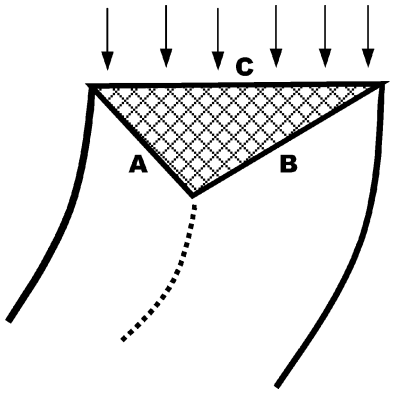


Figure 13 Growth model of the single-helix carbon coil A–C indicates different crystal faces of (000n).

yield was as small as 1.4 mol% by using WS_2 catalyst while as high as 10–15 mol% by using Ni catalyst as shown already. This may be caused by the different chemical activity of thiophene to different metal catalysts.

4. Conclusions

Very regular single-helix CMCs with a constant coil pitch and coil diameter were prepared by using WS_2 catalyst from gas mixture of acetylene, hydrogen and *t* hiophene as an impurity The optimum reaction temperature and thiophene gas flow rate was 780°C and 0.2 sccm. The fact that the coils are composed of two parts and the tip morphology indicate that only two rear crystal faces dedicate for the deposition of carbon.

Acknowledgements

This work was supported by the Grant-in Aid for the Innovative Technology (No. 13506) and the Grant-in Aid for Scientific Research (No. 13555171) of the Ministry of Education, Culture, Sports, Science and Technology, by Japan Society for the Promotion of Science (No. P02372).

References

1. W. R. DAVIS, R. J. SLAWSON and G. R. RIGBY, *Nature* **171** (1953) 756.

2. *Idem.*, *Trans. Brit. Ceram. Soc.* **56** (1957) 67.
3. R. T. K. BAKER, M. A. BARBBER, P. S. HARRIS, F. S. FEATES and R. J. WAITE, *J. Catal.* **26** (1972) 51.
4. R. T. K. BAKER, P. S. HARRIS and S.TERRY, *Nature* **253** (1975) 37.
5. R. T. K. BAKER and J. J. CHLUDZINSKI JR., *J. Catal.* **64** (1980) 464.
6. H. P. BOEHM, *Carbon* **11** (1973) 583.
7. S. MOTOJIMA, M. KAWAGUCHI, K. NOZAKI and H. IWANAGA, *Appl. Phys. Lett.* **56** (1990) 321.
8. S. MOTOJIMA, M. HIRATA and H. IWANAGA, *J. Chem. Vapor Deposition* **3** (1994) 87.
9. S. MOTOJIMA, S. ASAKURA, M. HIRATA and H. IWANAGA, *Mater. Sci. Eng.* B**34** (1995) L9.
10. S. MOTOJIMA, I. HASEGAWA and H. IWANAGA, *J de Physique, IV*, C **5** (1995) 1061.
11. S. MOTOJIMA, Y. ITOH, S. ASAKURA and H. IWANAGA, *J. Mater. Sci.* **30** (1995) 5049.
12. S. MOTOJIMA, S. ASAKURA, S. TAKEUCHI and H. IWANAGA, *Carbon* **3** (1996) 289.
13. S. MOTOJIMA and X. CHEN, *J. Appl. Phys.* **8** (1999) 3919.
14. X. CHEN and S. MOTOJIMA, *Carbon* **37** (1999)1817.
15. X. CHEN, S. MOTOJIMA and H. IWANAGA, *ibid.* **37** (1999) 1825.
16. *Idem.*, *J. Cryst. Growth* **237–239** (2002) 1931.
17. M. FUJII, M. MATSUI, S. MOTOJIMA and Y. HISHIKAWA, *ibid.* **237–239** (2002) 1937.
18. S. MOTOJIMA, H. IWANAGA, V. K. VARADAN, *Hyomen* **36** (1998) 140.
19. V. V. VARADAN, R. RO AND V. K. VARADAN, *Radio Sci.* **29**(1) (1994) 9.
20. F. GUERIN , V. K. VARADAN and V. V. VARADAN, *J. Wave-Material Interaction* **7**(4) (1992) 279.
21. Y. KATO, N. ADACHI, T. OKUDA, T. YOSHIDA, S. MOTOJIMA and T. TSUDA, *Jpn. J. Appl. Phys.* **42** (2003) 5035.
22. S. MOTOJIMA, unpublished data.
23. M. KAWAGUCHI, K.NOZAKI, S. MOTOJIMA and H. IWANAGA, *J. Cryst. Growth* **118** (1992) 309.
24. S. MOTOJIMA and X. CHEN, *J. Appl. Phys.* **85** (1999) 3919.
25. X. CHEN, T. SAITO, M. KUSUNOKI and S. MOTOJIMA, *J. Mater. Res.* **14** (1999) 4329.
26. W. T. OWENS, N. M. RODRIGUEZ and R. T. K. BAKER, *Catal. Today* **21**(1) (1994) 3.
27. T. KATO, K. KUSAKABE and S. MOROOKA, *J. Mater. Sci. Lett.* **13** (1994) 374.

Received 10 July
and accepted 24 November 2003