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Coiling-chirality changes in carbon microcoils obtained by catalyzed pyrolysis of acetylene and its mechanism

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As can be seen in the double helix of DNA, the single helix of proteins, etc., the three-dimensional (3D) helical/spiral structure is a fundamental structure of living things, and affords them critical functionalities. Helically coiled carbon fibers, which usually take the peculiar form of either a microcoil or a helix or twisted form, referred to as ‘‘carbon microcoils hereafter,’’ are of great interest due to their novel functionality and various potential applications. They can potentially be used in electromagnetic absorbers and/or filters, 3D composites, smart tunable electrical devices, microsensors, chiral catalysts, etc.
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In 1956, Davis *et al.* reported the vapor growth of two thin carbon fibers twisted together in the form of a rope.[1] Since then, some researchers have reported observations of spiral-form vapor grown carbon fibers. For example, Baker *et al.* reported the morphology of a spring-like branched carbon filament obtained in a Sn/Fe catalysis system.[2] Lee *et al.* observed twisted carbon nanofibers among carbon nanofibers grown on soda lime glass at 500 °C using thermal chemical vapor deposition.[3] Motojima *et al.* reported the preparation of carbon microcoils (CMCs) with micron- to nanometer-ordered coil diameters by metal-catalytic pyrolysis of acetylene containing a small amount of sulfur.[4–9]

The growth mechanism of the carbon microcoils is very interesting. In 1970, Boehm proposed a bottom growth mechanism for braided carbon filaments.[10] Amelinckx *et al.* proposed a formation mechanism of helix-shaped graphite nanotubes based on a spatial velocity hodograph.[11] Nakayama and co-workers proposed the difference effect of an In and Fe bicatalyst.[12] We proposed that the coiling driving force of the carbon fiber grown by catalyzed chemical vapor deposition (CVD) is the catalytic anisotropy of a catalyst crystal face related to carbon deposition.[13,14] However, the reasons why two coiling patterns, right clockwise (R) and left clockwise (L), formed have not been discussed, and the coiling-chirality mechanism is still not known. The coiling direction within a section of carbon coil is generally either right clockwise or left clockwise. Up to now, no helical/coiled carbon fibers with coiling chirality alternating between right clockwise and left clockwise within a coil section have been reported. We have found that, by using a catalyst, coiling chirality changing within a piece of coil grown by catalytic pyrolysis of acetylene could take place.

In this study, twisting carbon microcoils with fiber diameters of 0.3–1 μm and with changing coil chirality were first prepared by metal-catalyzed pyrolysis of acetylene. The preparation conditions, morphology, and microstructure of the carbon microcoils were examined, and then the mechanism of the changing coiling chirality was discussed.

A graphite or stainless steel (SUS 304) plate substrate was placed in a horizontal quartz reaction tube (600 mm in length and 40 mm in diameter). Fine powders of WS_2 and the SUS 304 stainless steel plate were used as the catalyst. Commercial acetone-dissolved acetylene was used as the carbon source. The reaction tube was heated to 700–800 °C using external electrical heaters, then acetylene, hydrogen, nitrogen, and thiophene gases were introduced into the reaction tube at flow rates of 30 mL/min (sccm) and 20–120, 40, and 10–0.05 sccm, respectively. A high-resolution ferroelectric-scanning electron microscope (FE-SEM) was used to examine the morphologies of the as-grown carbon coils.

Using a stainless steel plate as the catalyst as well as the substrate, carbon microcoils with a coil diameter of several microns and coil length of several millimeters were generally obtained. The carbon microcoils generally have a double helix form like DNA. The optimum reaction temperature, at which the maximum coil yield was obtained, was 775–785 °C. The optimum gas flow rates of acetylene and thiophene were 60 and 0.15 sccm, respectively. Among the common double helix carbon microcoils, a significant number of carbon coils of twisted single form were observed. Representative twisted carbon coils are shown in Fig. 1. The coil diameter of the twisted coils and the diameter of the carbon fibers from which the carbon coils formed are 1 and 0.6 μm, respectively. It is very interesting to observe that the twisting (coiling) direction of the coil changes from L to R (or R to L) at the point shown by the arrow. That is, the coiling chirality changes during the growth. Figure 2 shows the carbon coils with successively changing coiling directions from L to R (or R to L). Twisted carbon coils with

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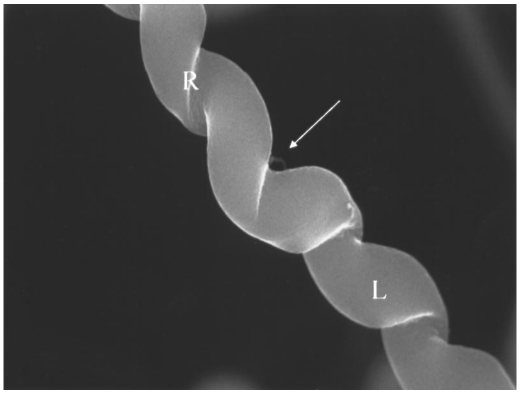

FIG. 1. Twisted carbon coils with changed coiling chirality. Catalyst: Stainless steel (SUS 304). The arrow indicates the location of the change in coiling chirality. (R) right-clockwise coiling; (L) left-clockwise coiling.

changing coiling chirality were also obtained using a Fe–Cr–Ni alloy with a small amount of other elements. Figure 3 shows that the carbon coil coiling chirality changed in the brighter part, i.e., the bent part shown by the arrow. Small amounts of Fe, O, and S as well as C were detected in this brighter part by electron probe microanalysis (EPMA), whereas Ni and Cr were not detected at all. That is, this brighter part is a Fe catalyst grain, and the coiling chirality changed at the location of this catalyst grain. This catalyst grain may be the growing point as in the case of the spring-like carbon microcoils obtained using the Ni catalyst. A catalyst grain with Fe_3C phase was generally observed on the tip of straight vapor grown carbon fibers (VGCFs) which were obtained using Fe as the catalyst and benzene as the carbon source at 1000–1100 °C. However, in this study, the crystalline phase of the brighter part has not yet been determined. On the other hand, the presence of Fe or other catalysts or impurity elements was not observed in the coiling-chirality-changed part of Figs. 1 and 2. This suggests that there are two coiling-chirality-changing mechanisms.

It was sometimes observed that a carbon fiber grew linearly and then twisted in the same direction to form twisted carbon coils (or twisted carbon coils grew and then stopped twisting or coiling to form a straight fiber) as shown in Fig. 4. The reasons why the straight fiber suddenly entwines and forms coils or why the coils stops entwining and form straight fibers are not known.

Using the WS_2 powder as the catalyst, the growth of twisted single carbon coils with changing coiling chirality as well as of general carbon microcoils of spring-like double helical form was observed. Figure 5 shows the branched carbon coils obtained using the WS_2 catalyst. The branched carbon coils have different coiling directions from the original coil as can be seen in Fig. 5(c). Furthermore, both coils of the original and branched coils also changed coiling chirality during the growth [arrow in Fig. 5(b)]. The growth of twisted carbon coils with the changed coiling chirality was more frequently observed than for that with the stainless steel catalyst. The presence of the catalyst or impurity elements was not observed in the branched part or coiling-chirality-changed part.

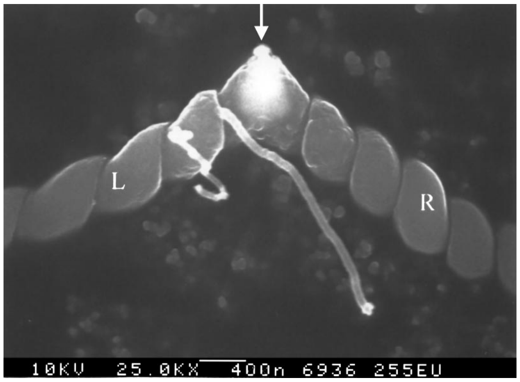

FIG. 3. Twisted carbon coils.

A well-formed catalyst grain was sometimes observed on the tip of carbon coils.[5,6] The catalyst grain is the exclusive growing point of the carbon coils. Using a Ni catalyst, the catalyst grain is a Ni_3C single crystal with different crystal faces, while a thin layer of Ni–C–S–O with an amorphous or solid solution phase is present on the surface of the Ni_3C crystal.[5] Different crystal faces with different chemical compositions have different catalytic activity for the growth of carbon coils. It is considered that the chirality of the catalytic activity of the catalyst grain strongly affects the chirality of the carbon coils grown and determines the coiling direction, right-clockwise coiling or left-clockwise coiling. That is, changing the coiling chirality may be caused by the changing catalytic activity of the catalyst grain. Similar situations may reasonably be considered for the case using stainless steel or WS_2 as the catalyst. Figure 6 shows a possible

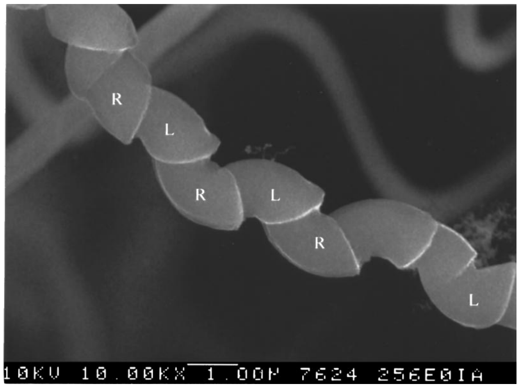

FIG. 2. Twisted carbon coils with changed coiling chirality. Catalyst: Fe–Cr–Ni alloy.

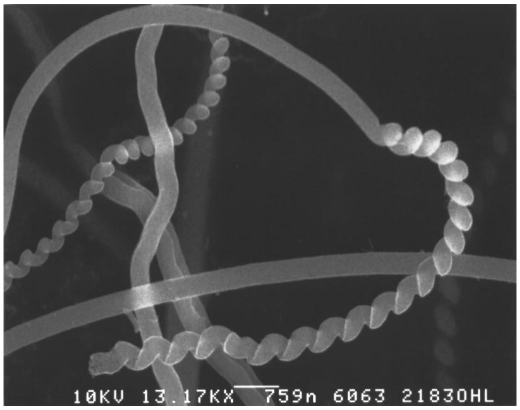

FIG. 4. Stopping the twisting (coiling) to form a straight fiber (or initiating the coiling to form a twisted coil).

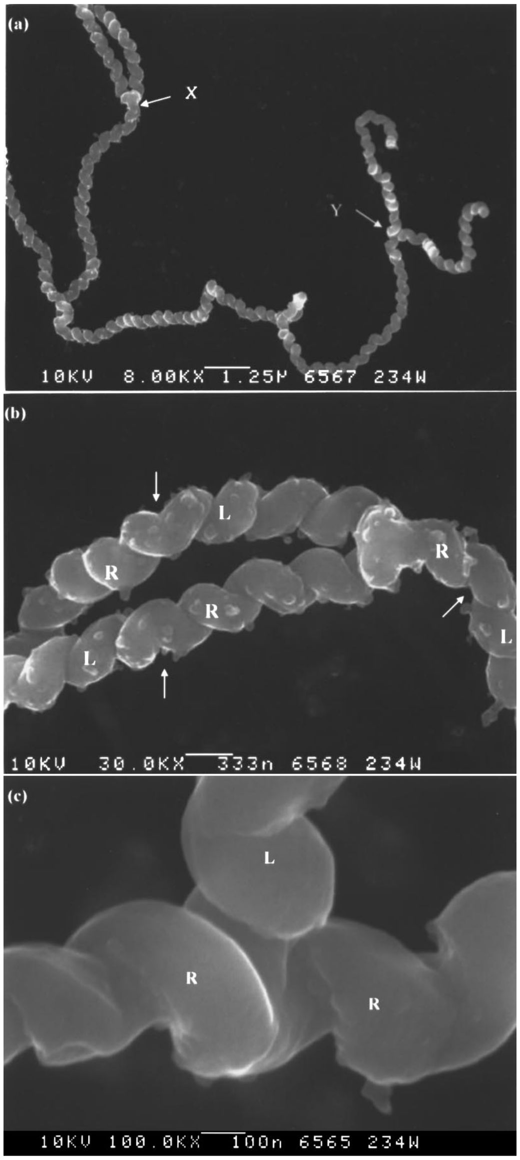

FIG. 5. (a) SEM images of branched twisted carbon microcoils, (b) enlarged view of arrow A in (a), (c) branched part and changing coiling chirality. Catalyst: WS_2. The arrow in (c) indicates the part changed by coiling chirality.

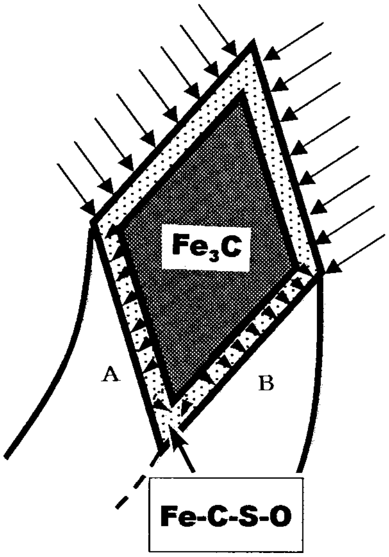

FIG. 6. 2D model for changing the coiling chirality.

two-dimensional (2D) model for changing the coiling chirality of the twisted carbon coils obtained using the stainless steel catalyst. In this 2D model, the following four hypotheses are postulated: (1) the catalyst grain present on the coiling-chirality-changed point is the Fe_3C crystal phase, (2) on this surface the Fe–C–S–O amorphous or liquid crystalline phase is present, (3) the higher S and O contents in the Fe–S–C–O phase, the higher the catalytic activity, and (4) crystal face B has higher catalytic activity than that of face A, and thus the carbon fibers grown curl toward the left. It is considered that a small amount of sulfur and oxygen is included in the carbon coils grown as in the case of the Ni catalyst.[14] The S and O are supplied from source gases via the Fe_3C catalyst grain and thin Fe–C–S–O layer. It is considered that the S and O content in crystal face A become smaller than that of crystal face B, and thus the catalytic activity of crystal face A decreases more than that of crystal face B with an increase of reaction time. This is caused by the fact that crystal face A has higher catalytic activity and thus a higher carbon deposition rate than crystal face B, resulting in a higher accompanying rate of sulfur and oxygen in the carbon deposited, and thus a higher decreasing rate compared with the supply speed. On the other hand, the sulfur and oxygen contents in crystal face B increase with an increase of reaction time, thus increasing the catalytic activity. At this point, the coiling chirality may change. However, other changing mechanisms of coiling chirality cannot be ruled out, and much research is needed to clarify the mechanism.

In conclusion, we prepared carbon microcoils with changing coiling chirality using stainless steel or WS_2 as the catalyst, and a changing mechanism based on changing the catalytic activity of the catalyst grain was proposed.

[1] W. R. Davis, R. J. Slawson, and G. R. Rigby, Nature (London) **171**, 756 (1953).
[2] R. T. K. Baker, P. S. Harris, and S. Terry, Nature (London) **253**, 37 (1975).
[3] C. J. Lee, T. J. Lee and J. Park, Chem. Phys. Lett. **340**, 413 (2001).
[4] S. Motojima, M. Kawakuchi, K. Nozaki, and H. Iwanaga, Carbon **29**, 379 (1991).
[5] S. Motojima, S. Asakura, M. Hirata, and H. Iwanaga, Mater. Sci. Eng., B **35**, L9 (1995).
[6] X. Chen, T. Saito, M. Kusunoki, and S. Motojima, J. Mater. Res. **14**, 4329 (1999).
[7] X. Chen and S. Motojima, J. Mater. Sci. **34**, 3581 (1999).
[8] X. Chen and S. Motojima, J. Mater. Sci. **34**, 5519 (1999).
[9] S. Motojima, M. Hirata, and H. Iwanaga, J. Chem. Vap. Deposition **3**, 87 (1994).
[10] H. P. Boehm, Carbon **11**, 583 (1973).
[11] S. Amelinckx, X. B. Zhang, D. Bernaerts, X. F. Zhang, V. Ivanov, and J. B. Nagy, Nature (London) **265**, 635 (1994).
[12] M. Zhang, Y. Nakayama, and L. Pan, Jpn. J. Appl. Phys., Part 2 **39**, L1242 (2001).
[13] S. Motojima and X. Chen, J. Appl. Phys. **85**, 3919 (1999).
[14] C. Kuzuya, W.-I. Hwang, S. Hirako, Y. Hishikawa, and S. Motojima, Adv. Mater., Chem. Vap. Deposition **8**, 57 (2002).