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Carbon nanocoils with changed coiling–chirality formed over Ni/molecular Sieves catalyst

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Carbon fibers with a helical form are receiving much attention recently because of their unique structures and their special mechanical and electromagnetic properties. Carbon microcoils, which usually take the peculiar forms, such as coiled-form, spiral-form, or twisted form, etc., in micron orders, are of great interest due to their novel functionalities and various applications. Potentially, they can be used in electromagnetic absorbers and/or fillers, 3D-composites, smart electrical devices, and in microsensors, etc. In 1956, Davis *et al.* [1] reported the vapor growth of two thin carbon fibers twisted together in the form of a rope. Since then some carbon filament researchers occasionally reported on the observation of carbon fibers with helical forms and discussed the growth mechanism [2–5]. Recently, more researchers reported the observation of helical carbon nanofibers [6–8]. However, the mechanism of coiling–chirality formation is still obscure. Up until now, no helical carbon fibers with changed coiling–chirality have been reported by other researchers except our report about twisted-shape carbon nanocoils with changed coiling–chirality using stainless steel and WS_2 as the catalysts [9].

In this article, tube-shaped carbon nanocoils with changed coiling–chirality, and the inner diameter of about 100 nm, were prepared by the Ni/molecular Sieves catalyzed pyrolysis of acetylene, the reaction conditions, morphology, and microstructure are presented.

Ni catalyst supported on the molecular Sieves was prepared by the impregnation method for incorporation of metal on molecular Sieves using reagent-grade nickel nitrate. The specific surface area of the catalyst was estimated to be 110.6 m^2/g by using a BET method. A horizontal tube (30-mm i.d., 700-mm length) was used as a reaction tube. The supported catalyst was set on the graphite plate substrate. A source gas mixture of C_2H_2, N_2, and an S-containing promoter was vertically introduced into the substrate surface from the upper gas inlet, and purged from the lower gas outlet. The gas flow rates of C_2H_2, N_2, and the promoter were fixed at 90×10^{-6}, 100×10^{-6}, and 5×10^{-6} m^{-3}, respectively. The flow rate of H_2 ranged from 10 to 300×10^{-6} m^{-3}; the reaction temperature and time were 750–800 °C and 30 min, respectively.

At lower hydrogen flow rate ($100–200 \times 10^{-6} m^{-3}$) very regular carbon microcoils with a coil diameter of below 2 μm were obtained after 30 min of deposition. The typical SEM image is given in Fig. 1, indicating that the carbon coils obtained are smaller in diameter than the carbon microcoils usually obtained by using an Ni micro-powder catalyst [4, 5]. With further decrease in hydrogen flow rate, as low as $20–50 \times 10^{-6}$ m^{-3}, tube-shaped carbon nanocoils with changed coiling–chirality were obtained. The SEM images in Fig. 2 show that the outer diameter is less than 1 μm. Furthermore, Fig. 3 gives the enlarged view of the nanocoils with various changed coiling–chirality patterns; it can be seen that the fibers are composed of two parts (arrow A and B). The direction of the coil axes tends to change along with changing coiling–chirality in such a pattern that the coil axes directions are roughly at 90°, in Fig. 3b, the coils are also quite long. The coiling–chirality changes may result in diversity of fiber patterns at the changed points, most of them are in the shape of "9" (Figs 3a and 4a), sometimes in the shape of "s" (Fig. 4b). In some cases, the coiling–chirality changes twice, e.g., from *L* (left-clockwise coiling) to *R* (right-clockwise coiling), then from *R* to *L*, as a result, the coiling–chirality is the same (*L*), but axis directions were changed.

An enlarged view of a coil surface is shown in Fig. 5, clearly indicating that the coil is a single-helix coil and is constructed by two parts, one part is bigger (shown by arrow A), the other part is smaller (shown by arrow B). The cross sections presented in Fig. 6 further confirmed this consideration. Fig. 7 shows the growth tip, suggesting that the coils are of one-directional growth type [10]. These morphologies are quite different from the morphology of double-helix carbon microcoils shown in our previous work [4, 5]. There are four characteristics for single-helix carbon nanocoils: firstly, the coiling–chirality and the direction of coil axis alternate frequently; next, their inner diameter is of nanometer size; then, they are of one-directional growth; and finally, the fibers are composed of two parts with different thickness. The two parts (A and B in Figs 5 and 6) of a carbon fiber combined in such a way that one is upon the other, and the interface is perpendicular to the coil axis, one part (A) is thick and the other part (B) is

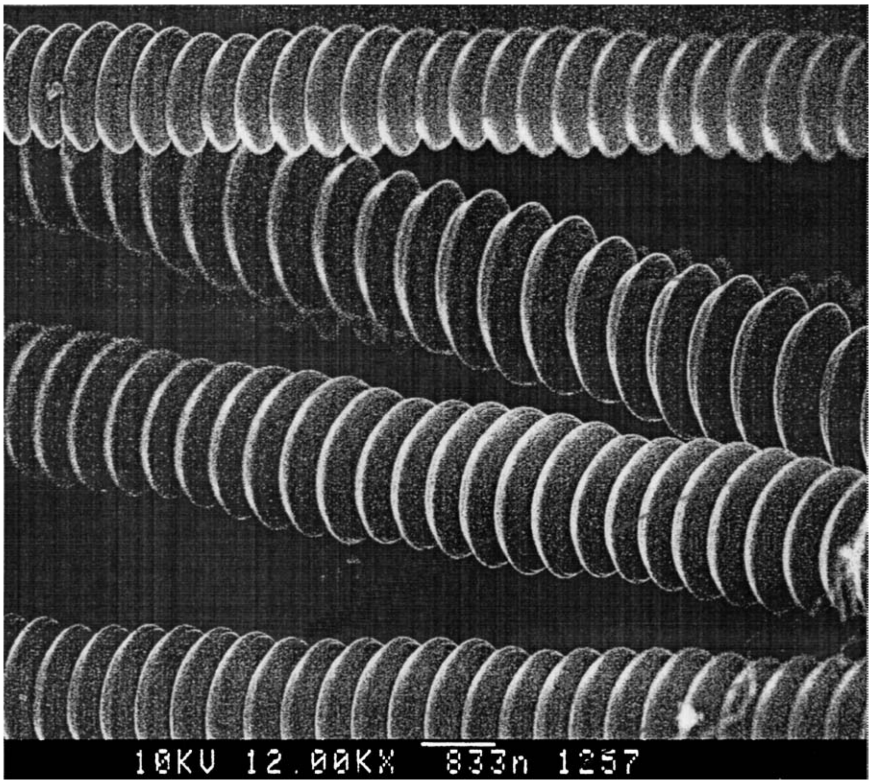

Figure 1 Typical regular carbon microcoils with an outer diameter of 1.5 micron.

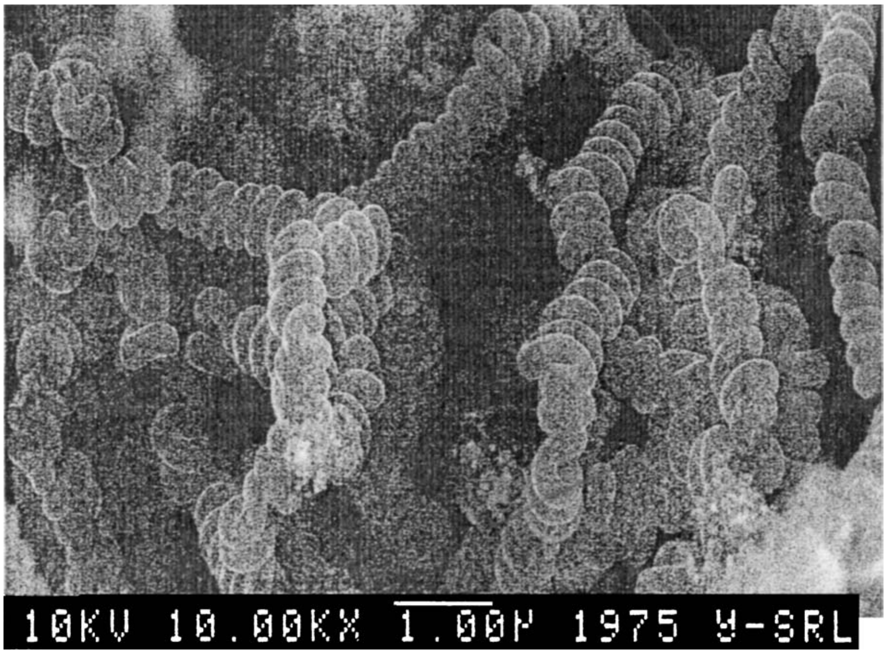

Figure 2 Typical carbon nanocoils with changed coiling chirality.

thin, the inner diameter is quite small (comparing with the outer diameter).

A growth tip of carbon microcoils grown over an Ni powder catalyst (our previous work), double-helix carbon microcoils with relatively large inner coil diameters of 5 μm are shown in Fig. 8. It can be seen that six fibers A_1, B_1, C_1, A_2, B_2, and C_2 grew from an Ni grain and coalesced to form two fibers X and Y, X and Y coiled in the same coiling direction. We have proposed a three-dimensional vapor growth mechanism for such kind of coiling patterns, on the basis of the anisotropy of catalyst faces, the growth speed of the three parts in the fiber X are different and in the order $A_1 > B_1 > C_1$, fiber C_1 is inside part, fibers $(A_1 + B_1)$ are outside (ref. 5). In this case, the cross-section area of the face A_1 is larger than that of B_1, and that of the face C_1 is smaller than that of A_1 or B_1. Therefore both fibers X and Y coil naturally curl to form double-helix carbon microcoils with large inner coil diameter. We refer to this coiling pattern as "anisotropic coiling patterns." This kind of coiling pattern could continue to grow up to 5–12 mm in coil length with constant

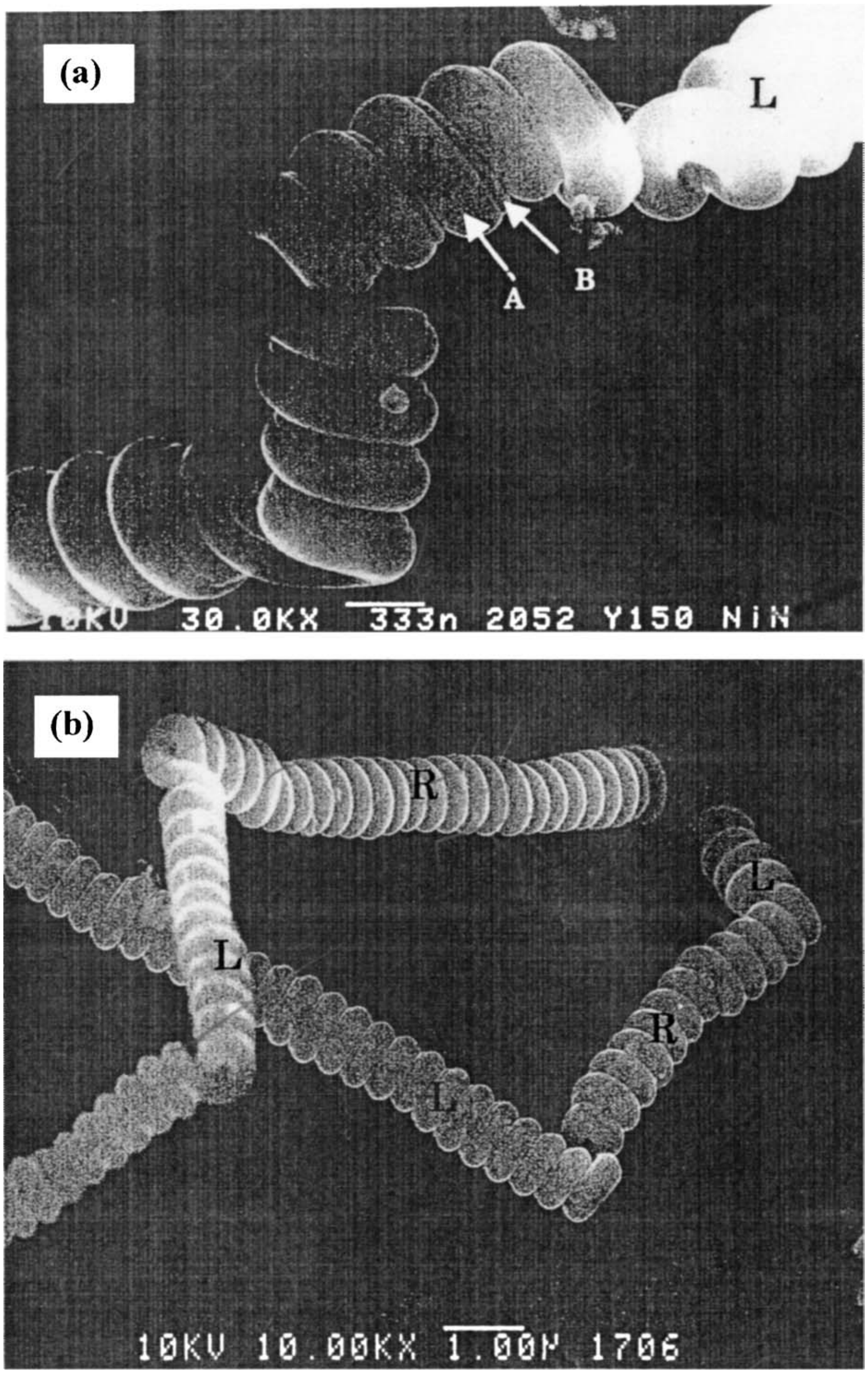

Figure 3 Various coiling–chirality-changing patterns.

coil diameter and constant pitch after a reaction time of 3–5 h. Until now, the changing in coiling–chirality has not been observed among these kinds of double-helix carbon microcoils. The tip part of the carbon microcoils have generally loosened-form as shown in Fig. 9a. Under these loosened conditions, carbon coils with regular coiling forms may not be obtained, while regular coils, occasionally may be obtained under tightly coiled tip as shown in Fig. 9b, these tips were rarely observed. This loosening of the coil tip may be caused by the steep decrease of the temperature as stopping the reaction and thus by releasing the inner stress by the loosening as can be seen commonly in the loosening of a steel spring. The regular coiling patterns observed beneath the loosened tip (Fig. 9a, arrow) may be caused by annealing out of the internal stress during some residence times at reaction temperatures. These phenomena may be a proof of the presence of internal stress in the coiled fibers while the origin of the stress is not yet known.

On the other hand, single-helix carbon nanocoils have generally very small or zero inner coil diameter caused by higher catalytic anisotropies between catalyst faces of the crystal grains than that of carbon microcoils with larger inner and outer coil diameter as shown in Figs 8 and 9. It is reasonably considered that this small coil diameter may result in high internal (intrinsic) stress between the inner and outer parts of the

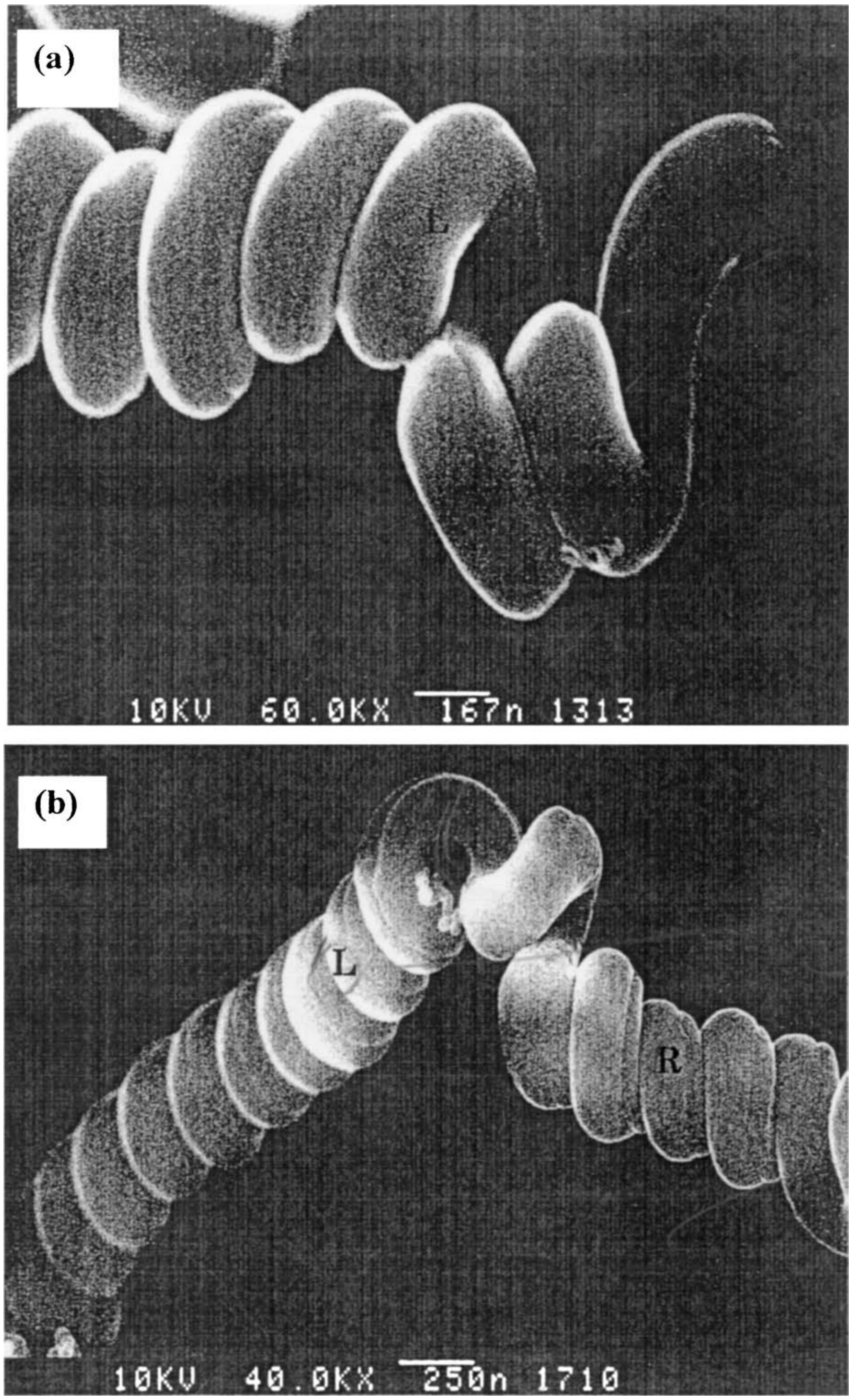

Figure 4 Enlarged view of various changed coiling–chirality patterns: (a) the changing point is of "9" shape, and (b) the changing point is of "s" shape.

coiled fibers, which may be caused by the large difference in the velocity of carbon deposition between the crystal faces. That is to say, the small coil diameter of carbon nanocoils may be maintained by this large internal stress. The internal stress may be increased with increasing reaction times and reach to critical value at last and then coiling direction may change for releasing this high internal stress. In this stage, very high internal stress may dominate the usual coiling driving force for a given direction by anisotropic properties of catalyst crystal faces, thus, coiling direction is forced to change. The changing coiling direction, coiling–chirality, may be caused by changing chemical composition, and thus changing anisotropic properties, in the thin layer of quasi-liquid phase present on the surface of catalyst grain, induced by very high internal stress. It may be considered that, without internal stress, changing anisotropic properties, which is caused by changing chemical composition in the thin layers present on the surface of the catalyst grain, can not occur quickly and thus the coiling direction cannot change quickly. Accordingly, we refer to these carbon nanocoiling patterns with changing coiling–chirality as "stressing coiling patterns."

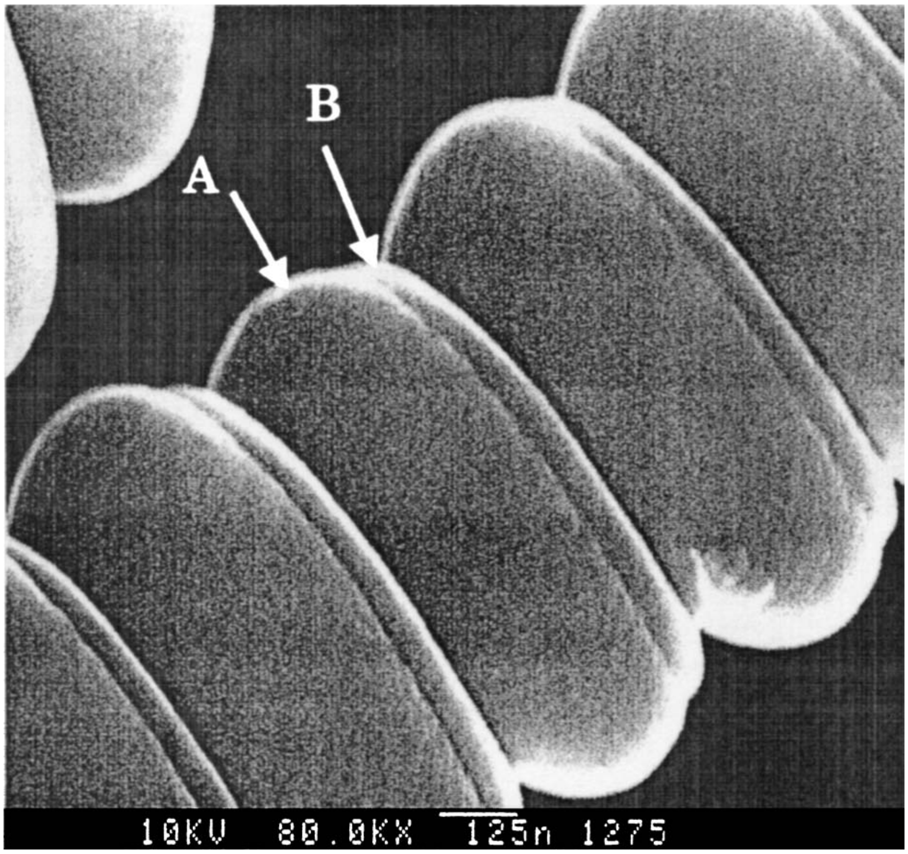

Figure 5 A typical enlarged view of the carbon nanocoil.

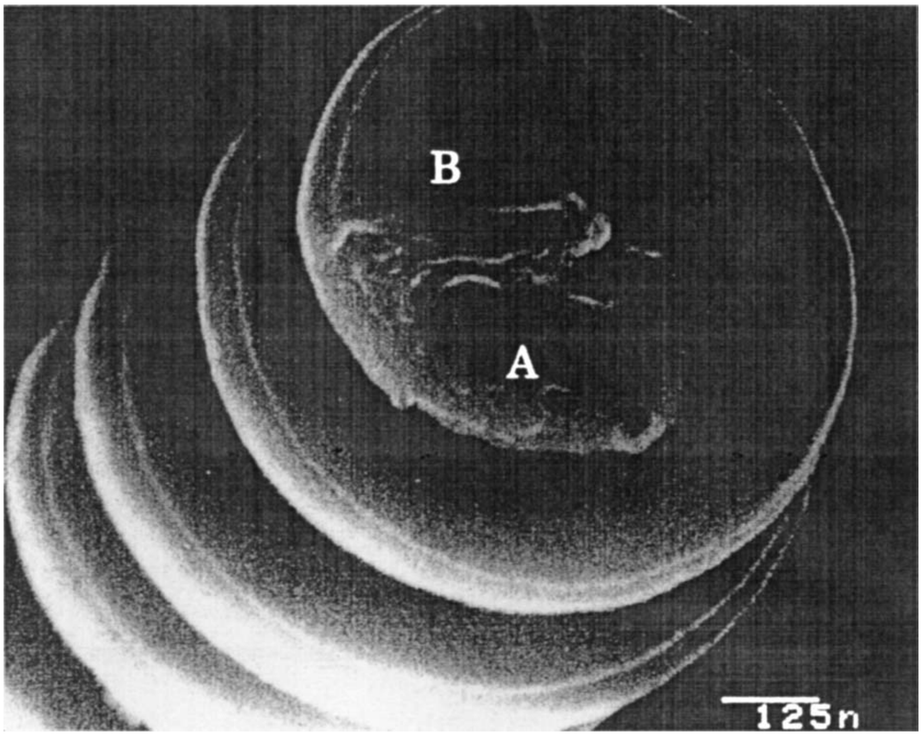

Figure 6 A cross section of the coiling–chirality-changing carbon coil.

Another reason for changing coiling–chirality was considered as the following: the carbon nanocoils with changing coiling–chirality were generally constructed from two parts, thick part (A) and thin part (B) as shown in Fig. 5. In this case it may be considered that the larger internal stress may be formed between interface of A and B, because of different cross section sizes of parts A and B, as well as between outer and inner parts along the coil axis. If the coil formed so that A (thick) was at the outside of the coil, and B (thin) was in the inside of the

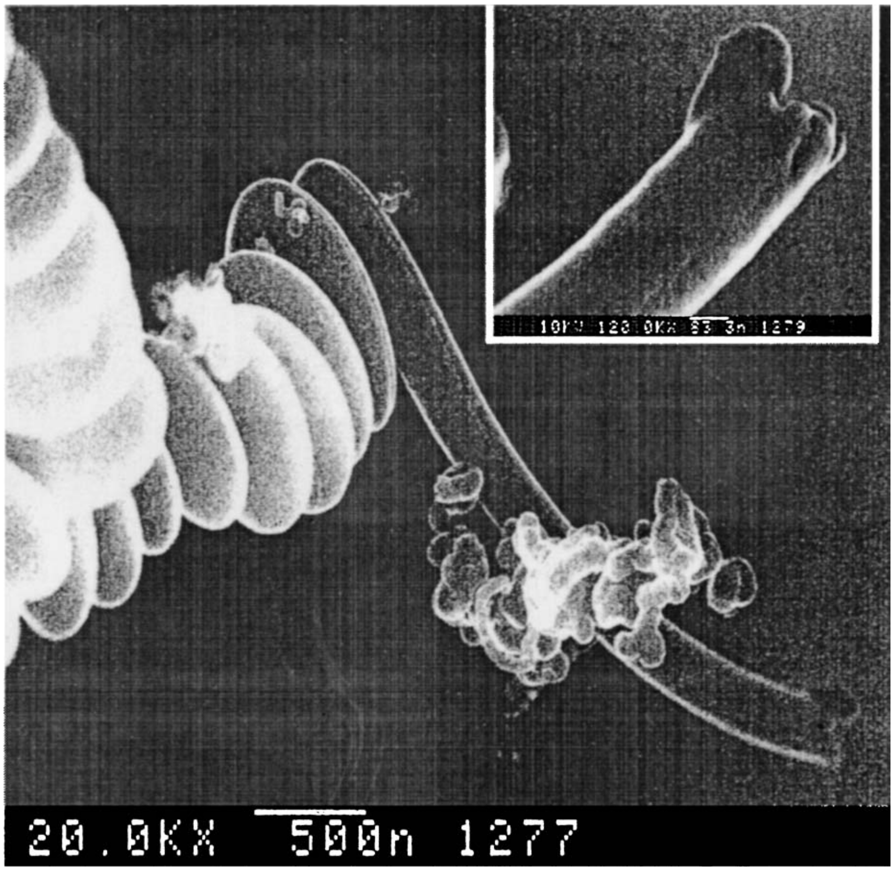

Figure 7 A growth tip of the coiling–chirality-changing carbon coil.

Figure 8 A growth tip of the double-helix carbon microcoil.

coil, the coiling–chirality change phenomenon would not happen, because there may be no stress along the coil axis.

The internal stress and different cross section sizes of A and B may be all affected by the reaction atmosphere, especially by hydrogen content, which may affect the hydrogen content in the catalyst grain as well as in the bulk fibers. Rodriguez [10] proposed that during catalytic growth of carbon nanofibers, hydrogen acts to enhance the reconstruction, which means some reactions happen in the catalyst grain such as $3Ni + C \leftrightarrow Ni_3C$, $Ni + H \leftrightarrow NiH_x$, etc., resulting in reforming the catalyst crystal grain to adapt the growth of carbon nanofibers. In this work, the flow rate of hydrogen is only about 1/20 of that for producing carbon microcoils with larger inner coil diameter than that of carbon

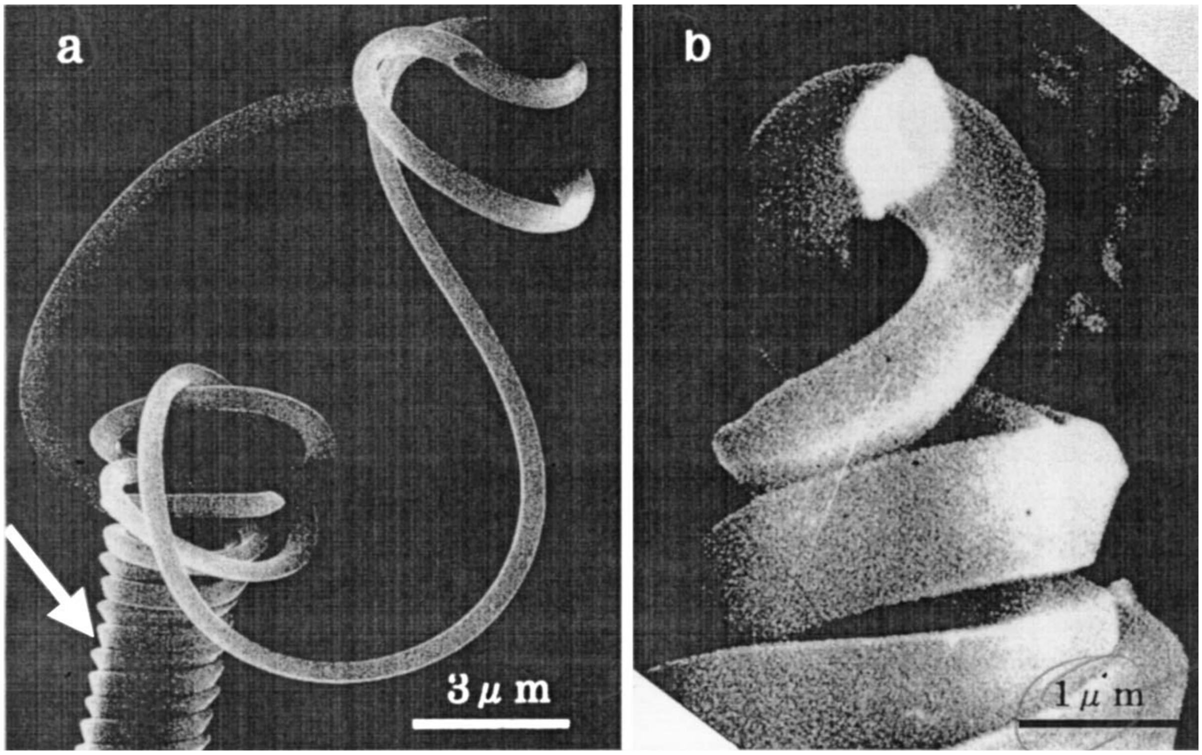

Figure 9 Loosened growth tip (a) and regular growth tip (b).

nanocoils. It is generally accepted that the presence of H_2 induces reconstruction of the exposed metal catalyst grain faces by weakening the metal–metal bond, leading to an induced mobility of surface atoms [10]. Thus, coiling stress is caused by low hydrogen feed.

In conclusions, tube-shaped carbon nanocoils with changing coiling–chirality were prepared by the Ni/molecular sieves catalyzed pyrolysis of acetylene at very low hydrogen feed. It is considered that the poor reconstruction of the catalyst grain caused the stressing coiling pattern, therefore, the coiling–chirality changes in order to release the coiling stress.

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