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Morphologies of carbon micro-coils grown by chemical vapor deposition

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The carbon micro-coils were obtained by the Ni-catalyzed pyrolysis of acetylene. The carbon micro-coils with various coiling morphology: regular double coils, coils built up by circular or flat fibers, super helix coils, single coils, etc. can be observed. The carbon coils with various coil diameters and coil pitches were obtained by controlling reaction conditions, such as reaction temperature, source gas flow rate of sulfur-impurity, acetylene or hydrogen.

1. Introduction

3D-helical/spiral-structure is the fundamental structure of all objects, this can be seen in the great maelstrom of the cosmos, in the α-helix of proteins, in double helix of deoxynucleic acid (DNA), screw dislocation in solid, vine plants, etc. Some researchers have tried to prepare 3D-helically micro-coiled fibers. For example, the growth and coiling morphology of carbon [1–9], SiC [10, 11] and Si_3N_4 [12, 13] have been reported. We have reported the preparation of regularly microcoiled carbon fibers by the catalytic 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 [14–16].

In this study, we prepared the carbon micro-coils by the Ni-catalytic pyrolysis of acetylene containing a small amount of thiophene and examined the coiling patterns and the morphologies in detail.

2. Experiment

The horizontal reaction tube (quartz, 1000 mm length, 60 mm i.d.), was heated from the outside by nichrome elements. The graphite plate, on which the Ni powder catalyst 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 nitrogen was introduced into the reaction tube through the upper gas inlets. The standard reaction conditions used are as follows: reaction temperature = 760–790 °C, gas flow rate of acetylene = 150–200 sccm, thiophene content in total gases = 0.6–0.8 mol %, gas flow ratio (H_2/C_2H_2) = 3–4.

3. Results and discussion

3.1. General morphologies of carbon coils

Under the standard reaction conditions, the carbon coils grew perpendicularly on the graphite substrate, pointing in the direction of the source gas inlets as shown in Fig. 1. A fine Ni catalyst grain (Ni_3C, rhombohedral) was always observed on a tip of the carbon coil. Almost all of the carbon coils prepared at the standard conditions are straight, double-coiled forms in which two fibers entwine with each other such as the double-helix of a DNA. The numbers of carbon coils having right-clockwise and left-clockwise coiled forms are about the same. Regular carbon coils with an average coil pitch of about 0.7 μm, an average coil diameter of about 5 μm, and a coil length of 5–8 mm can be obtained evenly on the substrate by 2-h reaction time. Representative regular carbon coils grown under the standard conditions by 2-h are shown in Fig. 2a. The cross-sections of the fibers that formed the carbon coils were generally circular or slightly elliptical forms (Fig. 2b), with the reaction time increasing, there are more fibers having flat cross sections (Fig. 2c). The forms of cross sections are considered to be roughly determined by the forms of the catalyst grains; the fibers with circular cross sections grow from the catalyst grains with coaxial forms and the flat fibers from elongated catalyst grains. Fig. 2d shows the SEM image of a coil which is at an extended state. The double helix structure can be seen more clearly by this SEM image.

Almost all of the carbon coils have double-helix micro-coil forms such as DNA as shown already. However, sometimes, a lot of interesting coiling morphologies were observed.

For example:

(1) Two fibers grown from a Ni grain (arrow in Fig. 3a) sometimes spiral separately (without entwining around each other), as a result, form a pair of single helical coils;

(2) the two fibers which formed the carbon coil not only grow at different speed, but also coil with no-coincident axis (Fig. 3b);

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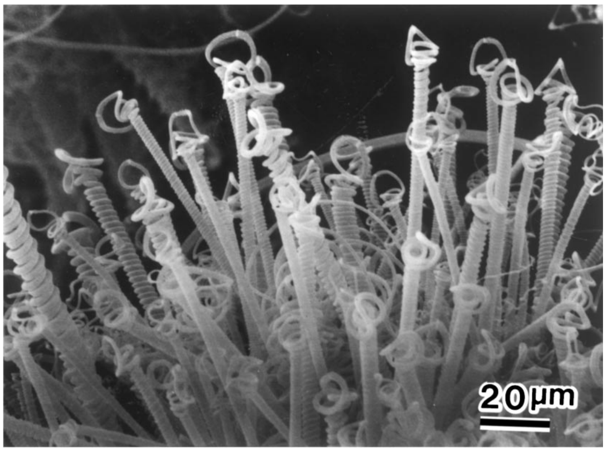

Figure 1 Representative as-grown carbon coils.

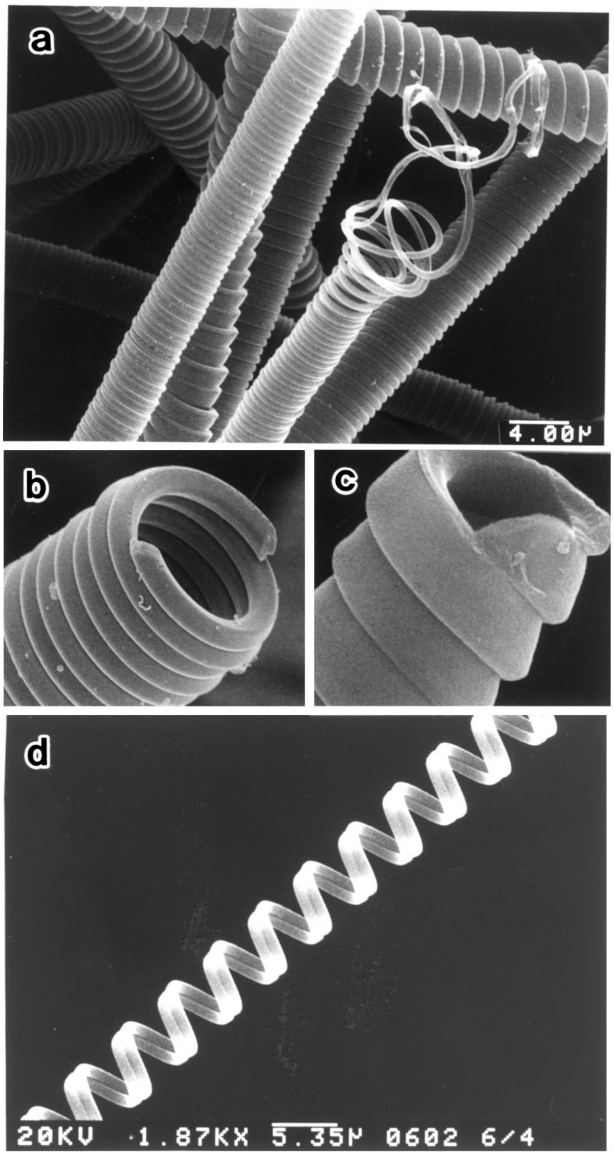

Figure 2 Representative morphology of carbon coils: (a) Regular coils; (b) circular coils; (c) flat coils; (d) extended state of regular coils.

(3) the two fibers formed carbon coil curl in different coil diameters (Fig. 3c);

(4) instead of straight coiling forms, but super helix forms of coils (Fig. 3d)

(5) insertion of one (or more) smaller coil into a larger coil (Fig. 3e).

3.2. Morphologies of carbon coils at different growth stages

Fig. 4a and 4b shows the SEM images of the carbon coils obtained at 5 and 15 min reaction time under standard conditions, respectively. It can be seen that carbon coils grown at the early reaction period (5 min) is very irregular, and the clear coil bodies have not been formed. The average diameter of the carbon coils is 13 μm, and the fibers that built up the carbon coils is thin with the average diameter of about 0.35 μm. Generally, with increasing reaction time, the carbon coils become regular-shapes. For example, both coil diameters and fiber diameters become relatively constant of 6 and 1 μm, at a reaction time above 1-h, respectively.

3.3. Controlling of morphologies by changing reaction conditions

Growth conditions, such as reaction temperature, source gas flow rate and ratios, reaction time, strongly affect the morphology and dimension of the carbon coils. In the other words, morphologies and dimensions of the carbon coils can be controlled by the reaction conditions.

a) Controlling of the lengths of the carbon coils

The carbon coils generally grow at the linear speed of about 1 μm/s in coil length. Accordingly, the carbon coils with different coil lengths can generally be prepared simply by controlling reaction times. But if the reaction time is above 3 h, the carbon coils will grow up to near the source gas inlets where the temperature was lower than the optimum one, and thus retarding the growth rate of the carbon coils. If the distance between the source gas inlets and the substrate is increased with increasing coil length, the carbon coil with 10–20 mm long after 6–10 h can be prepared.

b) Controlling of coil diameters: Larger coil diameters

The reaction temperature strongly affects the decomposition characteristics of acetylene; the kind of chemical species and their amount. On the surface of the Ni catalyst grain (Ni_3C single crystal), small amount of sulfur and oxygen as well as nickel and carbon are contained. The anisotropy of the carbon deposition on the respective crystal faces of the catalyst grain may be caused by the different contents of these elements on the respective crystal faces. The higher reaction temperatures may caused the larger deviation of the optimum sulfur content in the Ni-C-S-O quartenary compositions at which maximum anisotropy of carbon deposition for growing carbon coils with small coil diameter is caused. The smaller the anisotropy, the larger is the coil diameter, following at last formation of straight fibers for zero anisotropy. That is, the reaction temperatures strongly affect the anisotropy of the catalyst grain, and thus morphologies and dimensions of the carbon coils. By adjusting the reaction temperature lower than the

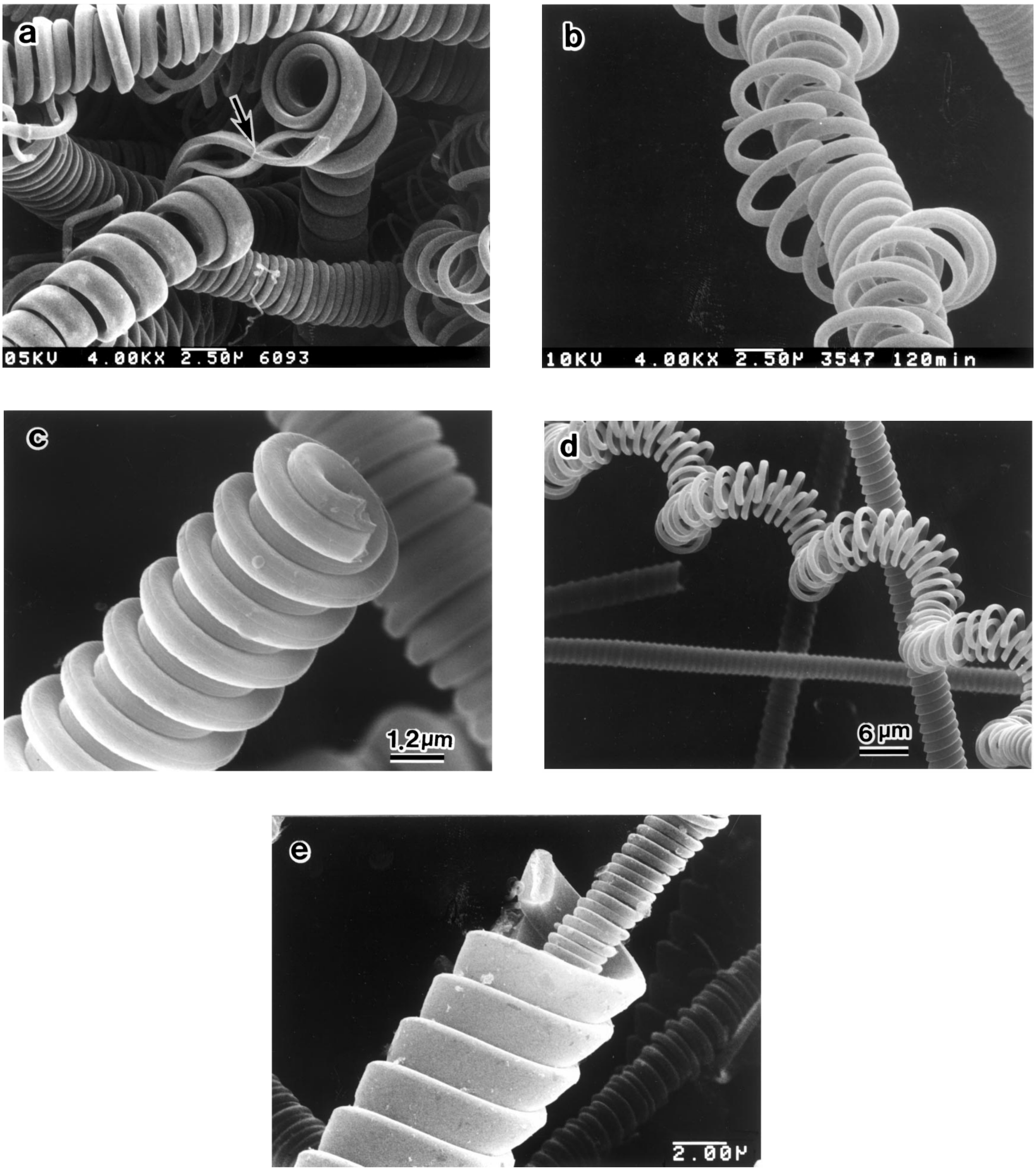

Figure 3 Various morphologies and coiling patterns of carbon coils: (a) Single coils, arrow indicates a Ni catalyst (Ni_3C) grain; (b) distorded double coils in which growth rate of one coil is faster than another coils; (c) double coils with different coil diameters; (d) super helix of double coils; (e) combination coils.

standard temperature (but larger than 730 °C), regular carbon coils with slightly larger diameters than 5 μm can be obtained (Fig. 5a). On the other hand, by controlling the reaction temperature higher than the standard temperature, such as 820 °C, irregular carbon coils with much larger coil diameters of 15–20 μm can be obtained (Fig. 5b).

c) Controlling of coil diameter: Smaller coil diameters

When the thiophene content in total gases was decreased, the grown carbon coils have generally smaller coil diameters. For example, if it is as low as 60% of the standard sulfur content, the carbon coils with coil diameters of about 3–4 μm were obtained as shown in Fig. 6. The thiophene content in total gas flow rate as well as reaction temperatures will strongly affect on the sulfur content in the Ni-C-S-O quartenary compositions and the anisotropy, and thus affect on the morphologies and dimensions of the carbon coils.

d) Controlling of both coil diameter and coil pitch:

SEM images of the carbon coils obtained at the lower acetylene flow rate of 50% than the standard one are shown in Fig. 7. Compared to Fig. 2a, it can be seen that carbon coils with larger coil pitches and larger

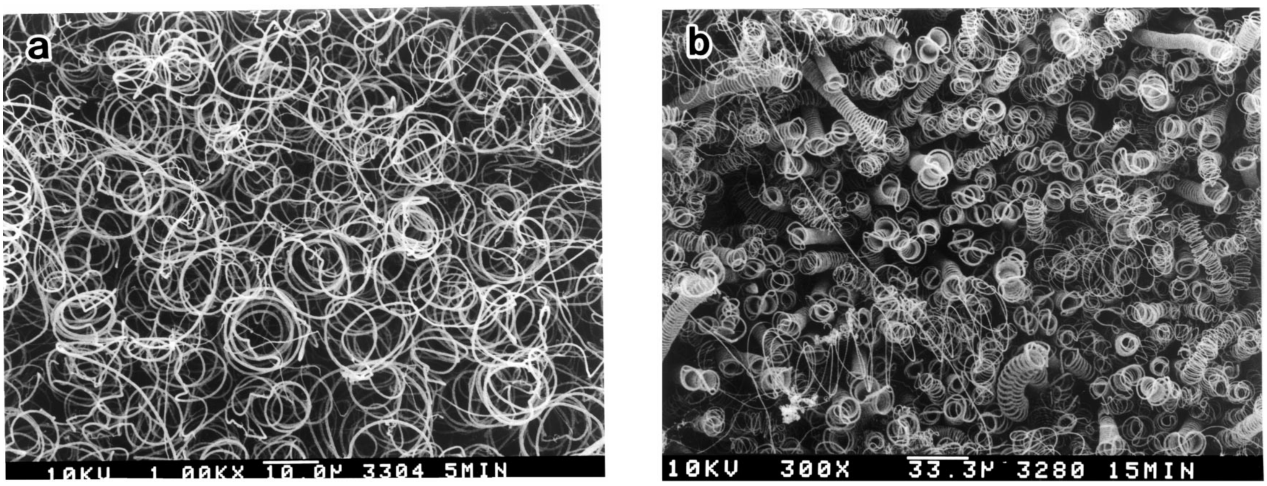

Figure 4 Carbon coils of initial growth stages. Reaction time: (a) 5 min; (b) 15 min.

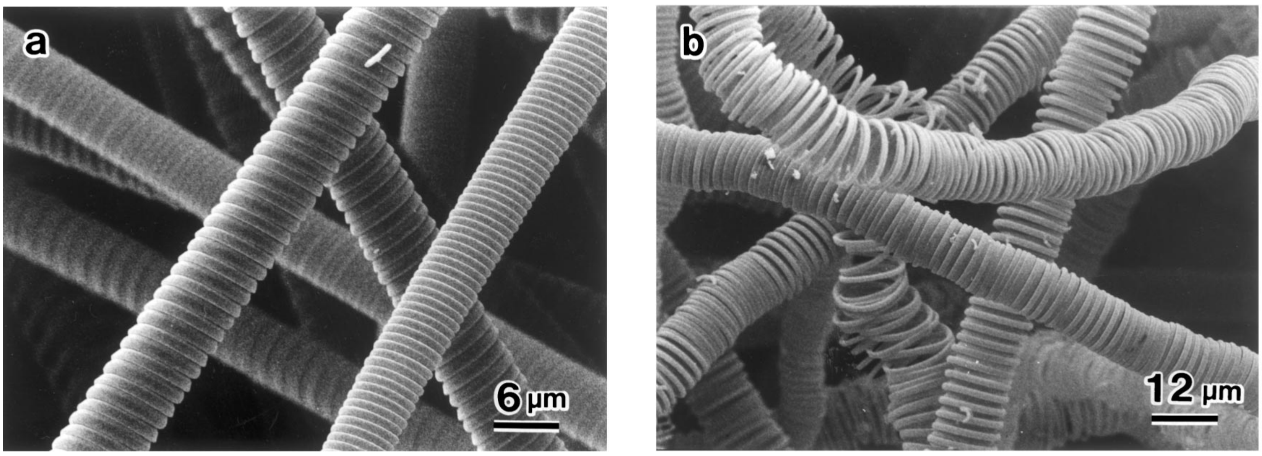

Figure 5 Effect of reaction temperature on the coil diameter: (a) Regular carbon coils with small coil diameter, reaction temperature = 750 °C; (b) carbon coils with larger coil diameter and slightly irregular forms, reaction temperature = 820 °C.

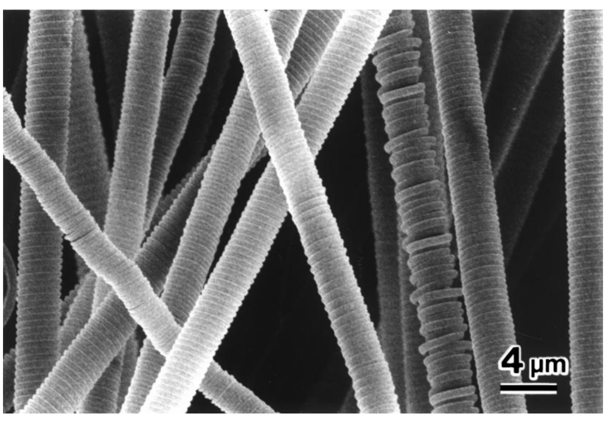

Figure 6 Effect of thiophene flow rate on the coil diameter.

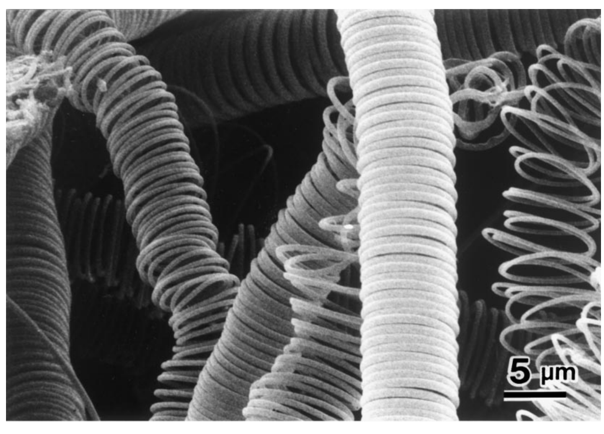

Figure 7 Effect of acetylene flow rate on the coil diameter and coil regularity.

coil diameters as well as less regularity than that prepared under the standard conditions can be obtained by decreasing the acetylene flow rate. This is because lower acetylene flow rate decrease the carbon content in the Ni-C-S-O quartenary compositions, thus affect the anisotropy. Furthermore, higher or lower flow rates of hydrogen than the standard conditions caused the increase of coil diameters and decrease of coil regularity.

3.4. Tip morphology and growth mechanism

Fig. 8 shows the enlarged views of the coil tips of carbon coils obtained at different reaction time, in which the arrows indicate Ni catalyst grains. A Ni catalyst grain was always observed on the tip part of the carbon coil, and morphologies of the tip part change with increasing reaction time. It was observed that interesting beard-like

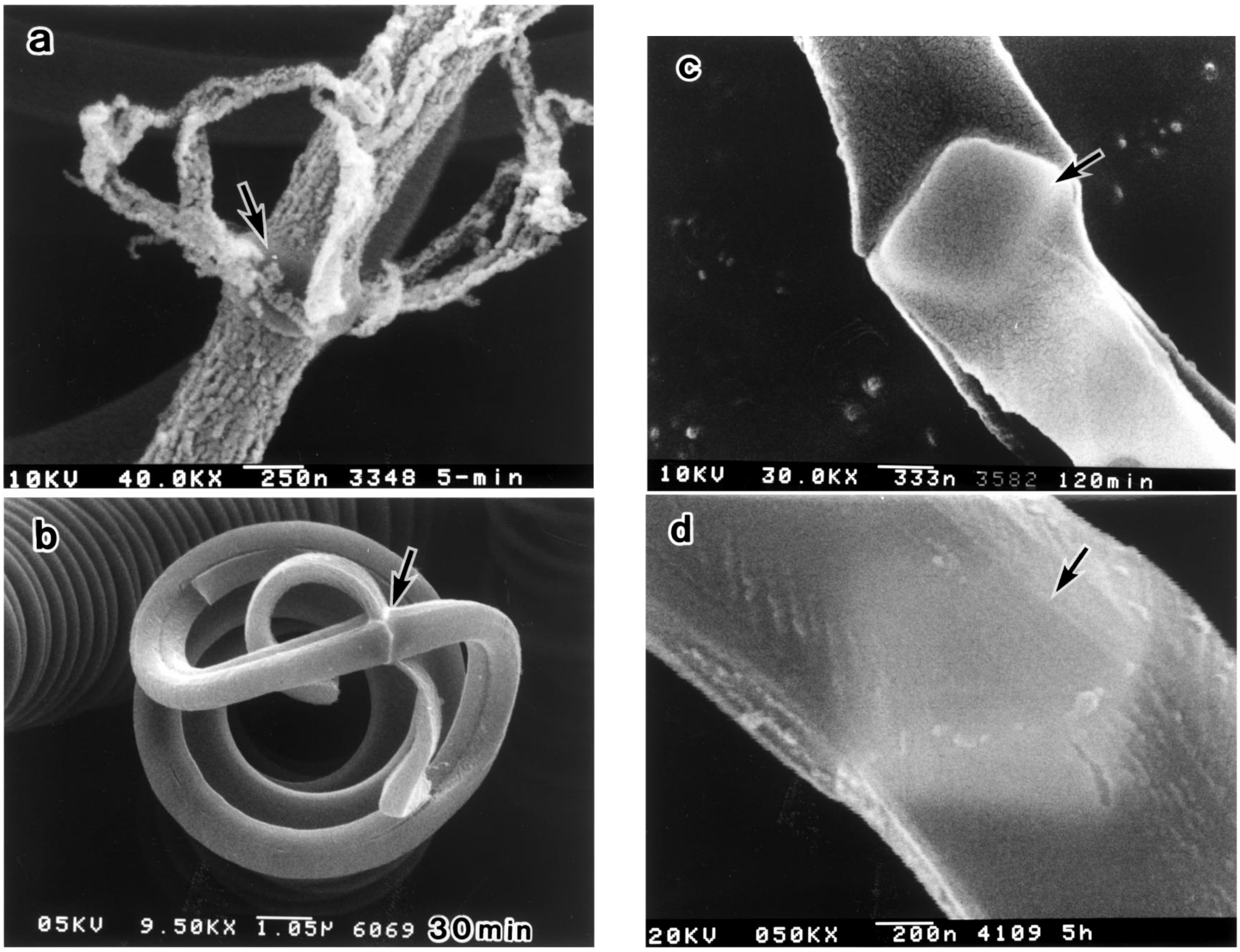

Figure 8 Tip morphologies of the carbon coils. Arrow indicates a Ni catalyst grain (Ni_3C). Reaction time: (a) 5 min; (b) 30 min; (c) 2 h; (d) 5 h.

deposits grew from the Ni catalyst grain for 5-min reaction time (Fig. 8a). The carbon particles deposited on the surface of growth tip are large for 5-min reaction times, with the increase of reaction time, the surfaces become relatively smooth. For carbon coils obtained at 5–30 min reaction times, six fibers frequently grow from six crystal faces of a hexahedral Ni catalyst crystal faces, among which respective three fibers coalesce together to form two fibers. These two fibers usually spiral (coil) in the same coiling direction, at the same coil diameter, and at the same growth rate of about one cycle per second around the coil axis. As the results, the growth rate of the carbon coils is about 1 μm per second, and that of the fibers that formed the carbon coils is about 7 μm per second.

The growth tips of '8'-shape was usually observed in the carbon coils prepared at above 15 min reaction time, and the Ni catalyst grain was buried within the carbon fibers with increasing reaction time as shown in Figs 8c and 8d.

3.5. Microstructure

The carbon micro-coils have no pore in the fiber axis of the carbon fiber which construct the micro-coils, and is full-filled to the core with very fine carbon grains of 20–100 nm diam [16]. Furthermore, the as-grown carbon micro-coils is almost amorphous state as was shown by X-ray diffraction analysis and Ramman spectra [17]. These microstructure of the carbon micro-coils are very different from that coiled carbon nanotube [18]. The reason of these structural characteristics of the carbon micro-coils are not yet known.

4. Conclusions

Regular carbon coils with a constant and small coil diameter of 5 μm and coil pitch of 0.7 μm, and coil lengths of 5–8 mm, can be obtained under the following standard reaction conditions; reaction temperature = 760–790 °C, reaction time = 2 h, thiophene content in total source gases = 0.6–0.8 mol %; C_2H_2 flow rate = 150–200 sccm; gases ratio (H_2/C_2H_2) = 3–4. The carbon coils with various coiling morphology; regular double coils, single coil, circular and flat coils, super helix coils, etc. can be observed. The coil diameter, coil pitch, and coil dimension of the carbon coils can be controlled by controlling reaction conditions.

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