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Materials Research Bulletin 43 (2008) 735–742
Materials Research Bulletin
www.elsevier.com/locate/matresbu

Effects of the size of nano-copper catalysts and reaction temperature on the morphology of carbon fibers

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Received 5 February 2007; received in revised form 15 March 2007; accepted 21 March 2007
Available online 24 March 2007

Abstract

In this study, carbon fibers with different morphologies, including coiled carbon nanofibers and straight carbon fibers, were obtained by the chemical vapor deposition using a Cu-catalytic pyrolysis of acetylene at 250 °C. The influences of nano-copper catalyst particle size and the reaction temperature on the morphology of carbon fibers were investigated. Under the same reaction condition, coiled carbon nanofibers generally were synthesized using nano-copper catalyst with smaller particles size, and bigger copper particles are apt to produce straight carbon fibers. With decreasing of reaction temperature to 200 °C, straight carbon fibers were obtained, instead of coiled carbon nanofibers at 250 °C. The product was characterized by field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and X-ray powder diffraction (XRD).

Keywords: A. Amorphous materials; B. Vapor deposition; C. Electron microscopy

1. Introduction

The related material of nanotubes, which was discovered by Iijima [1], carbon fibers attracted the attention of many scientists in the wide fields of science and nanotechnology as an important component in the realization of nanotechnology due to their outstanding mechanical and electromagnetic properties, surface properties, etc. With the appearance of various forms of carbon fibers such as whisker-like, branched, bi-directional, spiral, coiled, many kinds of carbon fibers growth models and mechanisms were established and discussed [2–10].

In order to investigate further the growth mechanism of carbon fibers, many researchers studied the influence of reaction conditions on the morphology of carbon fibers. Motojima and coworkers [11] reported that the yield of carbon fibers decreased by 35–50% due to the substrate rotation and irregular carbon coils were obtained, while regular coils were obtained without rotation. The influences of temperature and gas environment on the morphology of carbon deposition were studied by McCaldin et al. [12], they suggested that the type of carbon deposited is affected by the initial CVD deposition conditions, and changing the CVD environment during deposition only alter the rate of

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doi:10.1016/j.materresbull.2007.03.022

deposition but not the type of carbon deposited. The role of hydrogen in this system is so important that it can encourage the growth of filamentous carbon.

Recently, nano-copper catalysts were used to catalytically synthesize carbon fiber and carbon nanotube [13–16]. In this contribution, we have studied the effect of nano-copper catalyst particles size and reaction temperature on the morphology of carbon fibers with the use of different catalysts and different reaction temperatures.

2. Experimental

2.1. Catalysts preparation

In this paper, three catalysts were used for the preparation of carbon fibers, the preparation methods of catalysts as follows.

2.1.1. Copper tartrate catalyst precursor (A)

Hundred milliliters of potassium sodium tartrate aqueous solution (0.0586 mol/l) was slowly added to 100 ml of 0.0586 mol/l copper dichloride aqueous solution under vigorous stirring, copper tartrate (light blue precipitate) was formed quickly and then filtered and washed with anhydrous ethanol, dried for 1 h at 100 °C.

2.1.2. Nano-copper catalyst (B)

The preparation of nano-copper (B) was carried out with hydrogen-arc plasma method. This method was described in detail in Ref. [17].

2.1.3. Nano-copper catalyst (C)

Firstly, 2 g sodium hypophosphite and 1.5 g gelatin were added to 60 ml distilled water, and prepared 100 ml of 0.625 mol/l cupric sulphate aqueous solution and 100 ml of 1.25 mol/l sodium hypophosphite aqueous solution, respectively; Secondly, the three kinds of solutions were heated to 85 °C; Lastly, the cupric sulphate solution and the sodium hypophosphite solution were slowly added to a container at the same rate under vigorous stirring, the precipitate was filtered and washed with distilled water and anhydrous ethanol in turn.

2.2. Sample preparation

In the present work, a horizontal quartz tube (9 cm in diameter and 90 cm in length) was used as the reaction tube. The catalysts, placed on a ceramic substrate, were located in the central part of the reaction tube, and the carbon fibers were obtained by the catalytic decomposition of acetylene at 250 °C for 30 min, the pressure within the reaction tube was atmospheric. At last, the reaction tube was cooled in a vacuum (5 Pa) to room temperature.

In addition, we have successfully synthesized carbon fibers at 200 °C for 1 h using copper tartrate as a catalyst precursor to investigate the effect of reaction temperature on the morphology of carbon fibers.

2.3. Sample characterization

FE-SEM micrographs were obtained with a cold field emission scanning electron microscope (FE-SEM, JEOL, JSM-6700F), operating at 5 kV at a working distance of 8 mm; transmission electron microscopy (TEM) was carried out on a JEOL JEM-2000EX at an accelerating voltage of 160 kV; X-ray powder diffraction (XRD) patterns were recorded on a Philips X'Pert MPD diffractometer with Cu Kα radiation (λ = 1.5418 Å).

3. Results and discussion

Fig. 1A shows a FE-SEM image of copper tartrate catalyst precursor (A), which has many parallel cracks in its sides. The inset (scale bar: 100 nm) displays a TEM image of the thermal decomposed product of copper tartrate catalyst precursor (A) obtained at the same temperature as acetylene polymerization reaction. From this TEM image,

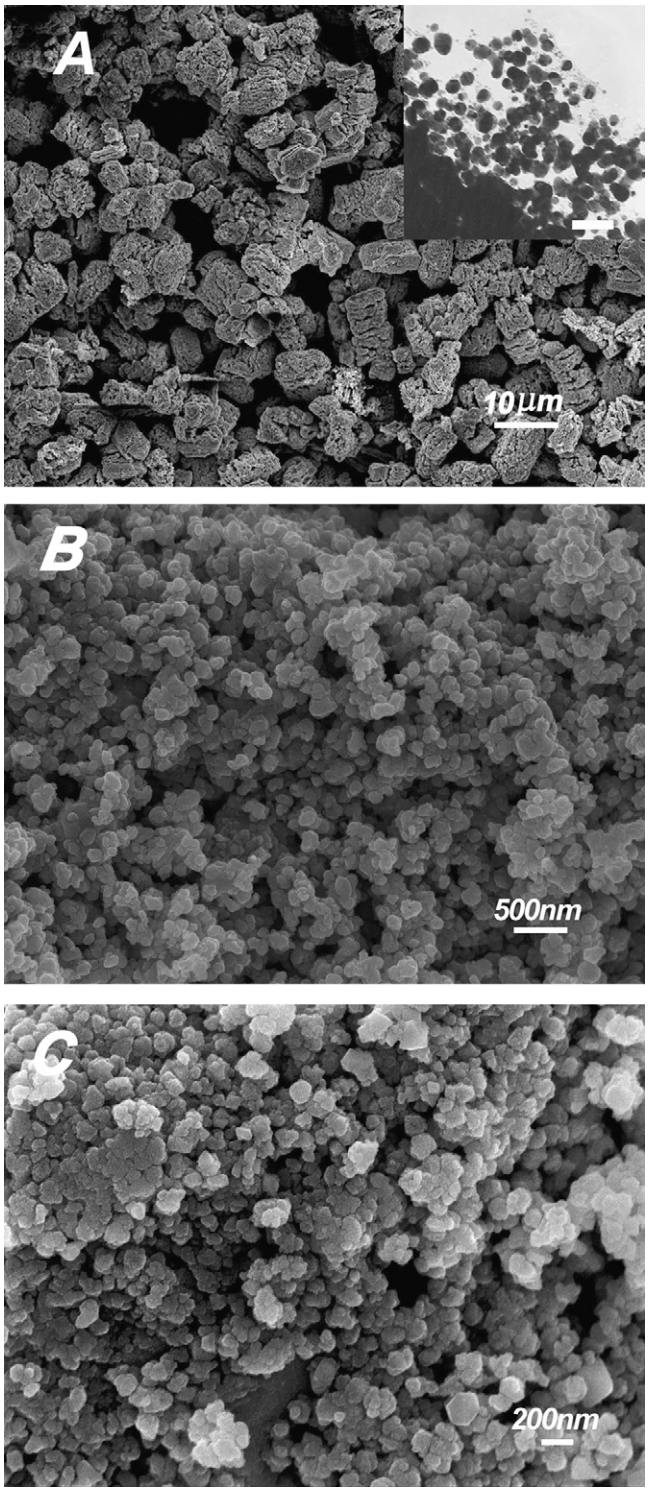

Fig. 1. FE-SEM photos of copper catalysts. (A) Copper tartrate precursor; (B) nano-copper; (C) nano-copper. The inset in (A) TEM photo of the thermal decomposed product of copper tartrate precursor.

we have found that the size of the decomposed product was ranged in 30–60 nm, smaller than that of nano-copper catalyst (B) particles, which is or above 120 nm. Nano-copper catalyst (B) particles, as shown in Fig. 1B, have uniform size, smooth surface, and exist as spheres or approximate spheres. Fig. 1C displays the morphology of nano-copper catalyst (C), the size of particles ranging from 60 to 110 nm.

It is well known that metal catalysis is the key for the formation of carbon fibers, and the physical and chemical characters of catalyst have an intimate relation with the morphologies of fibers.

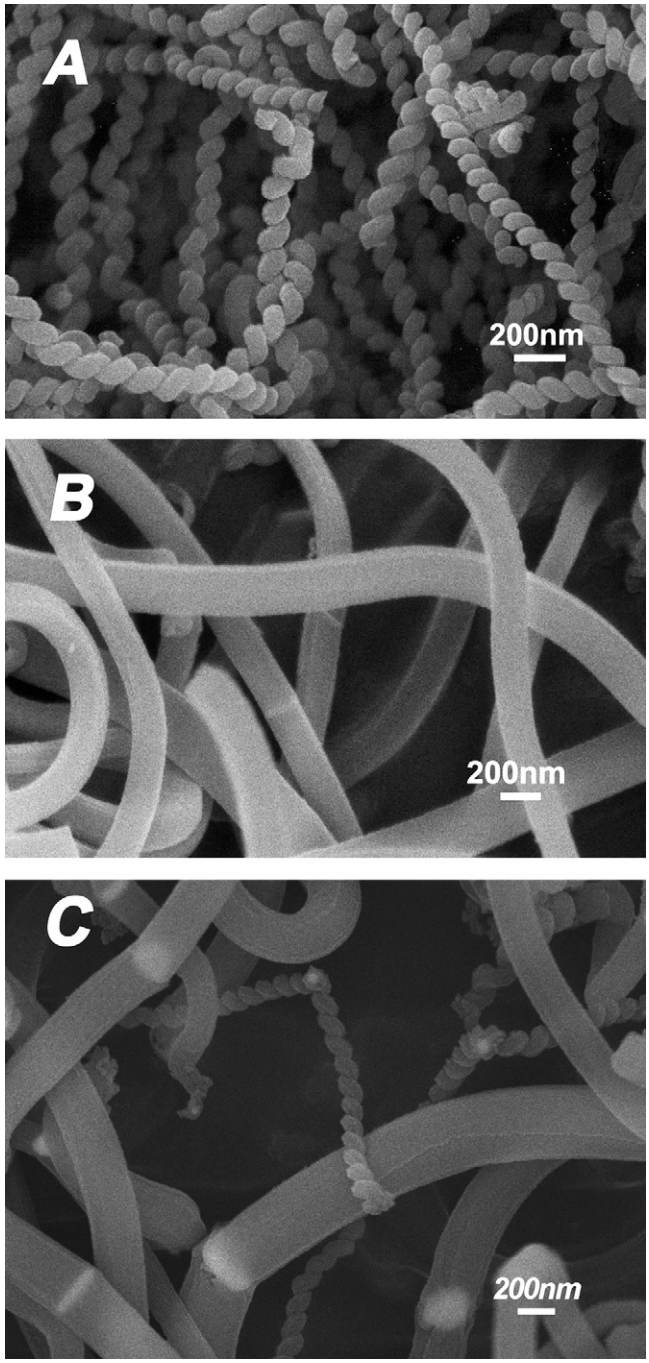

Fig. 2. Coiled carbon nanofibers (A), straight carbon fibers (B), the mixture of coiled carbon nanofibers and straight carbon fibers (C).

The synthesis reactions of carbon fibers were carried out using the above-mentioned three kinds of catalysts. It was observed that coiled carbon nanofibers were obtained using copper tartrate catalyst precursor (A) as a catalyst precursor, as shown in Fig. 2A. On the other hand, we have prepared straight carbon fibers over nano-copper catalyst (B) particles. Interestingly, nano-copper catalyst (C) can catalytically synthesize coiled carbon nanofibers and straight carbon fibers at the same time.

From a previous publication [18], we known that the shape of catalyst particles included in carbon fibers has an influence on the morphologies of carbon fibers, but the extent of which is limited, that is, the shape of catalyst particles is not determined factor to the morphology of carbon fibers [19].

In this study, we found that the morphology of carbon fibers is related to the size of catalyst particles, namely, the smaller catalyst particles are apt to synthesize coiled carbon nanofibers and the bigger ones to straight carbon fibers. Then, nano-copper catalyst (C), including smaller particles and bigger ones, can prepare coiled carbon nanofibers and straight carbon fiber simultaneously.

In order to investigate the relation between the morphology of carbon fibers and the size of catalyst particles in more detail, we have observed the morphologies of carbon fibers using nano-copper catalyst (B) as a catalyst after the growth period 3 and 15 min, respectively. Fig. 3A shows a FE-SEM image of the carbon fibers prepared at 250 °C for 3 min, a mass of nano-copper catalyst (B) particles can be observed obviously, which was coated with a layer of carbon. When increasing reaction time from 3 to 15 min, the typical carbon fibers, shown in Fig. 3B, were synthesized

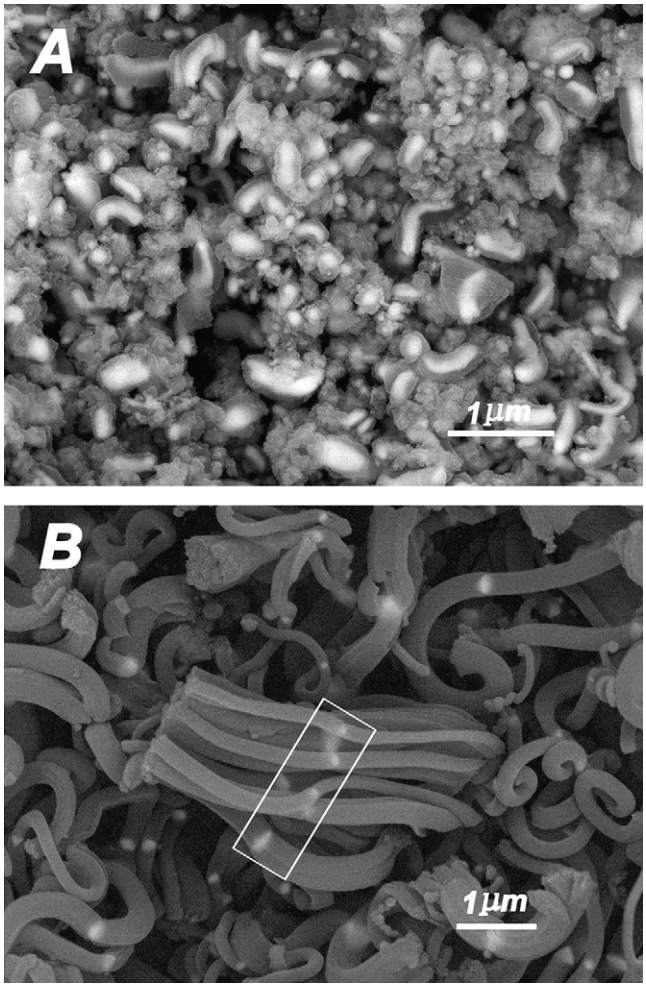

Fig. 3. FE-SEM photos of carbon fiber synthesized for different reaction periods: (A) 3 min; (B) 15 min.

at 250 °C, and the growth rate of carbon fibers is about 4.5 nm/s. An interesting phenomenon is that catalyst particles in carbon nanofibers bundles are almost in the same plane (rectangular area in Fig. 3B), which indicates that the cluster of catalyst particles were coated into a agglomeration during the initial growth period of carbon fibers; with the continuing growth of carbon fibers, the inner stress among fibers, which generated from the different growth directions of carbon fibers, became stronger and stronger until the catalytic particles were separated slowly, then typically straight carbon fibers formed.

From the XRD patterns of carbon fibers, as shown in Fig. 4A and B, we know that both samples have the same components, the sharp peaks and the disperse peak correspond to the nano-Cu catalyst and carbon fibers, respectively. XRD analysis showed that there was a difference in the relative content of metal Cu and carbon in both samples.

In addition, the straight carbon fibers were prepared successfully where the copper tartrate was used as a catalyst precursor, and the reaction temperature and reaction time in this experiment are 200 °C and 1 h, respectively. The morphologies of the prepared carbon fibers are shown in Fig. 5. The growth rate of carbon fibers is about 0.5 nm/s. One possible explanation is that the growth rate of carbon fibers, as a result of the lower reaction temperature 200 °C, is so slow that the agglomeration of catalyst particles were formed even before the start of the carbon fibers growth effectively, and the agglomeration of catalyst particles behaves isotropy to the growth of carbon fibers, so straight carbon fibers have been synthesized, not coiled carbon nanofibers.

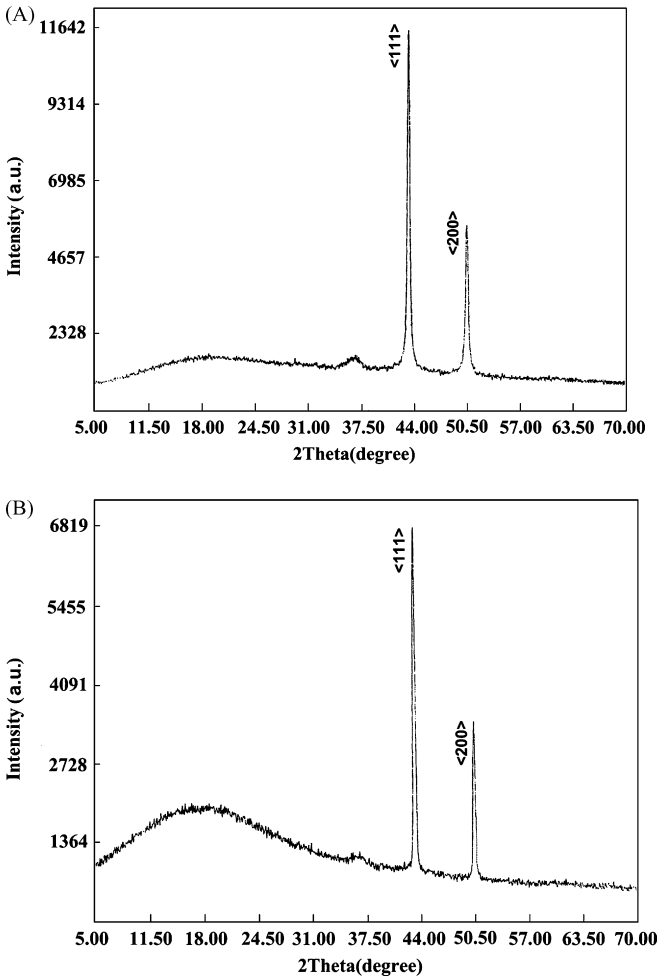

Fig. 4. XRD patterns of carbon fibers for different reaction periods: (A) 3 min; (B) 15 min.

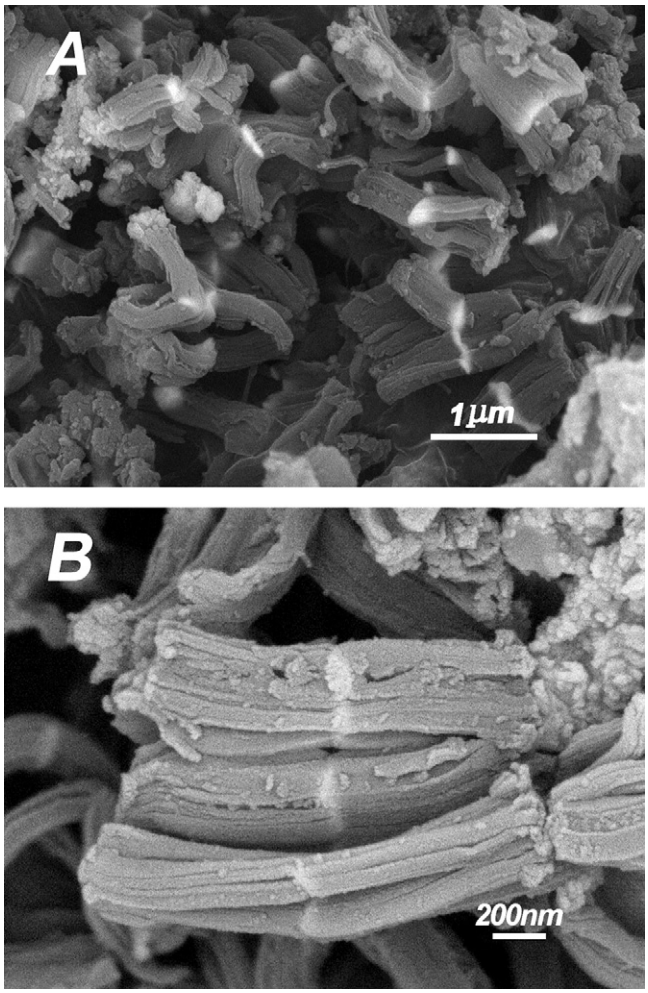

Fig. 5. FE-SEM photos of straight carbon fibers prepared using copper tartrate as a catalyst precursor at 200 °C for 1 h.

4. Conclusion

In our work, we have successfully synthesized straight carbon fibers and coiled carbon nanofibers using nano-copper as a catalyst. The influence of catalyst particles size on the morphology of carbon fibers has been investigated and discussed, that is, the smaller catalyst particles are apt to synthesis coiled carbon nanofibers, the bigger ones to straight carbon fibers. Straight carbon fibers, not coiled carbon nanofibers, will be obtained at 200 °C using copper tartrate as a catalyst precursor, lower than typical reaction temperature 250 °C.

Acknowledgment

The Natural Science Foundation of Shandong Province supported this work financially.

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