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CARBON NANOCOILS PREPARED BY THE CATALYTIC PYROLYSIS OF ACETYLENE

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[Abstract] The carbon microcoil/nanocoils are a kind of vapor grown carbon fibers with specific regular 3D-helical/spiral conformation and amorphous structure. In this study, the morphologies, as well as the microstructures of carbon nanocoils obtained by catalytic pyrolysis of acetylene using a serious of Fe-containing catalyst and WS_2, are presented.

Key words: carbon nanocoil, acetylene, iron catalyst, nickel catalys

1. Introduction

Recently, low dimensional nanomaterials such as nanotubes [1-3], nanowires[2], or nanorods [3-5] are at the forefront of materials science because those materials have many potential applications such as nanoelectronic devices, hydrogen absorption materials, etc. The relating research work play an important role in understanding some fundamental concepts, for example, the effects of dimensionality, morphology, chirality and microstructure of the nanomaterials on optical, electronic, electromag- netic, magnetic, optical and mechanical properties.

On the other hand, the so-called catalytic decomposition of hydrocarbons or carbon monoxide disproportionation, or chemical vapor deposition (CVD) process, which stand on the chemistry of solid–gas reactions on a metallic surface, are the only viable solutions offering less energy consumption and easy scaling up compared to other production methods, such as the electric arc discharge or laser ablation of graphite. By this method, various carbon nanomaterials with different structures and conformations such as carbon naonotubes, carbon nanofibers, can be obtained, especially by acetylene pyrolysis over Fe-group catalysis [6-12].

The carbon microcoil/nanocoils are a kind of vapor grown carbon fibers with specific regular 3D-helical/spiral conformation. Although helical carbon nanofibers were occasionally observed by carbon filament researchers [9-12], carbon microcoil /nanocoils have not been extensively reported by other reasearchers until Motojima found that the three-dimensional helix/spiral carbon microcoils could be obtained by the catalytic pyrolysis of acetylene. We have reported on carbon microcoils prepared by Ni-catalyzed pyrolysis of acetylene [13-18]. We also found that Fe was not a suitable catalyst for the growth of carbon microcoils. However, recently, we developed a series of catalysts and obtained various kinds of carbon nanocoils with different coiling pattern by the catalytic pyrolysis of acetylene in the CVD process. The carbon nanocoils are expected to be used in novel nanosensors or actuators.

In this study, the morphologies , as well as the microstructures of carbon nanocoils obtained by catalytic pyrolysis of acetylene using a series of Fe-containing catalysts and WS_2 are presented.

2. Experimental

A vertical quartz tube (6×10^{-2}m, i. d.), which has an upper source gas inlet and a lower gas outlet, was used as the reaction tube. Catalysts such as (1) Fe-Cr-Ni-Mo-Sn alloy; (2) Fe-Cr-Ni-Sn; (3) Fe- Cr-Ni; (4) Au-coating stainless plate; (5) WS_2 powder were used as the catalysts, on the graphite substrates, and were set in the center of the reaction tube. The quartz reaction tube was heated by nichrome element from the outside. A source gases mixture consisting of acetylene and hydrogen, hydrogen sulfide, and nitrogen was vertically introduced onto the substrate surface through the upper gas inlet and exhausted through lower gas outlet; the pressure within the reaction tube is atmosphere. The reaction temperature were 650-800℃, gas flow rates of acetylene, hydrogen, nitrogen and hydrogen sulfide-hydrogen were 60~100, 15~200, 100, and 5-20 sccm respectively.

3. Results and discussion

3.1 Twisted single-helix carbon nanocoils and zigzag nanofibers

It was found that when using an alloy catalyst Fe-Ni-Cr-Mo-Sn at the reaction temperature of between

650~800℃, thick carbon fiber formed on the substrate, the twisted carbon nanocoils were formed together with the zigzag carbon nanofibers on the thick carbon fiber after a reaction time of about 10 mins. Fig.1 shows that carbon nanocoils co-grew with zigzag nanofibers and straight carbon fibers; the enlarge view shows the nanofiber coiled tightly without coil gap.

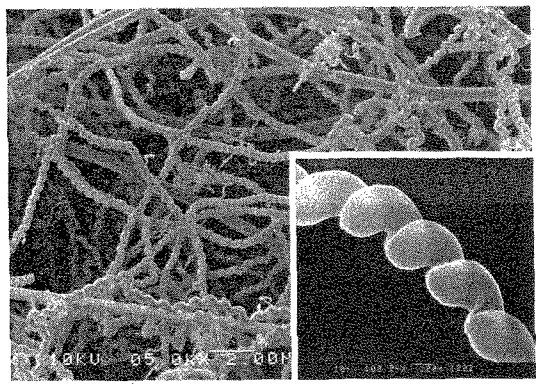

Fig. 1 As-grown twisted carbon nanocoils, with zigzag nanofibers co-existing.

Fig.2. give SEM images, which show that the carbon microcoils and twisted carbon nanocoils co-exist, these images provide a good comparision between nanocoils and microcoils. In Fig.2a, the carbon microcoil is a flat carbon coil [18] with fiber width of about 1 μm and a coil diameter of about 5 μm, while the twisted nanocoil has a outer diameter of about 300 nm; in Fig.2b, the carbon microcoil is a circular carbon coil [18] with fiber width of about 0.5 μm and a coil diameter of about 3 μm, while the nanocoil has a outer diameter of about 800 nm. It is noted that in Fig.2b the inner coil diameter is more larger than the fiber diameter rather than zero.

In contrast to carbon microcoils described in Ref. 17, also as shown in Fig.2, the morphology characteristic of twisted carbon nanocoils is that the coil inner diameter is quite small or zero. In addition to the characteristic of the small inner diameter, their outer coil diameter is several hundred nm, slightly larger than the fiber diameter. their length is as small as several microns after a reaction time of 30 mins.

The catalyst crystal grain of pear-like shape usually presents on a coil tip, from which two fibers originated bi-directionally and continuously curled to form the carbon nanocoil (Fig.3), these two fibers are with opposite twisting chirality, e.g., right-hand and left-hand twisting. It is very interesting to observe the phenomena that along with one fiber (without a growth tip), alternating of chirality or alternating from twisting-form to straight-form, or, from straight-form to twisting-form are common (Fig. 4).

Fig. 5 shows the enlarged view of the carbon nanocoil's ruptured cross section, no pore is observed in the central part

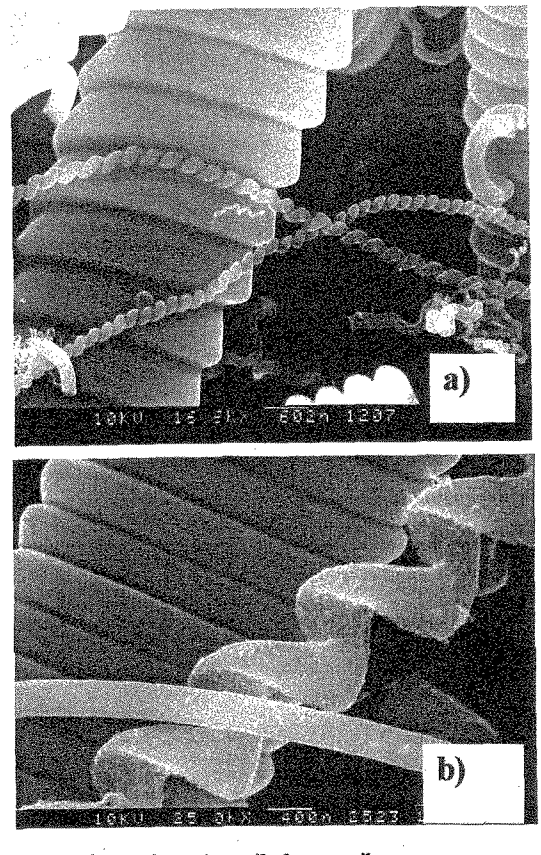

Fig.2 carbon microcoils & nanocoils.

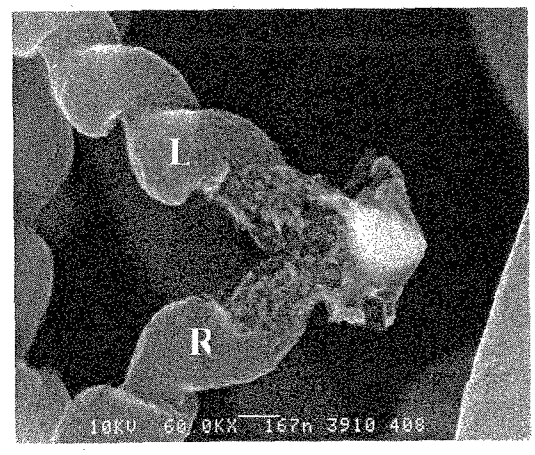

Fig. 3 Growth tip & chirality of the twisted carbon nanocoils.

of the fiber axis, it can also be seen that the carbon grains are concentrically oriented. A TEM image is given in Fig. 6, showing that the structure is more order than carbon microcoils described in ref. 15, that is, the graphite crystalline of the carbon nanocoils obtained in this work are

higher than carbon microcoils.

The morphology of the zigzag carbon nanofibers are shown in Fig. 7. It can be seen that zigzag nanofibers are always composed of two twin fibers, curling with a regular and continuous s-shape, 2-dimensionally and periodically, just similar to wave-motions. A striation or continuous dent is observed along the fiber axis on the middle part of the fiber. The zigzag fiber are actually of chirality alternating continuously two-dimensionally. But the formation mechanism is still unclear.

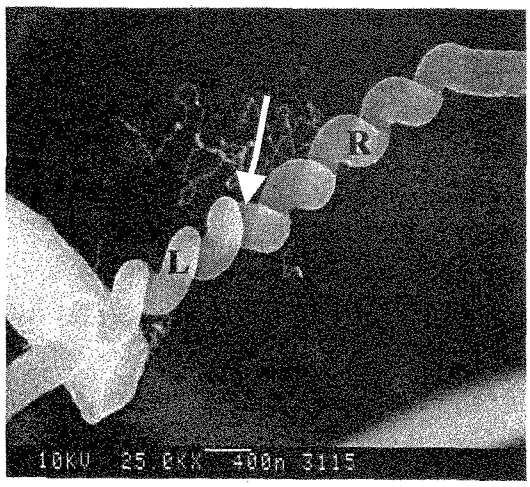

Fig. 4 A twisted carbon nanocoil with chirality changing.

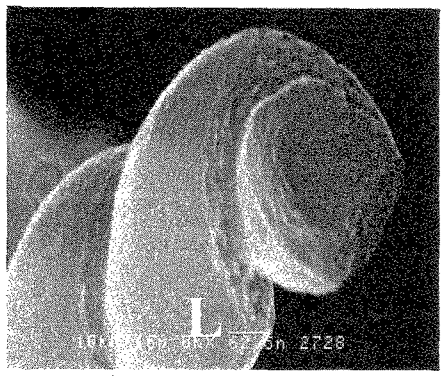

Fig. 5 A cross section of a L-twisted carbon nanocoils.

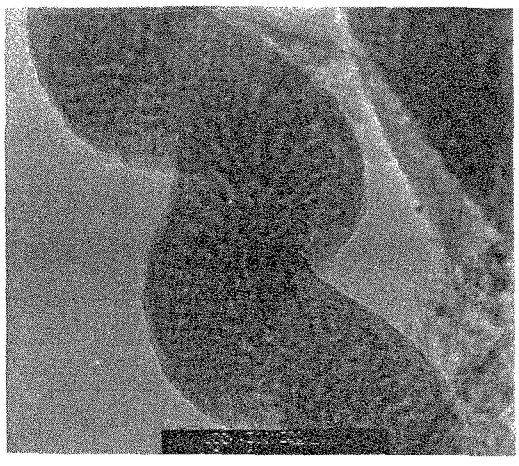

Fig. 6 TEM image of twisted carbon nanocoil.

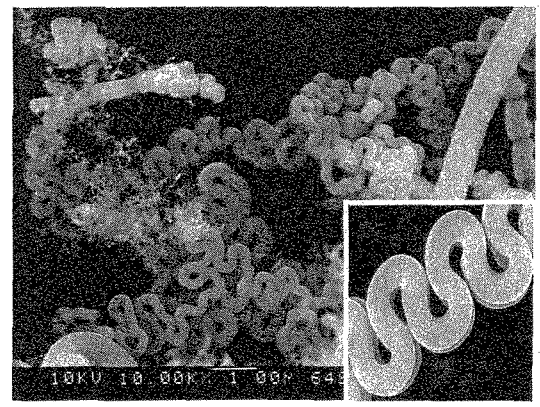

Fig. 7 zigzag nanofibers.

3.2 Double-helix carbon nanocoils

By using an alloy catalyst, Fe-Cr-Mo-Sn (without Ni) at the reaction temperature of 750℃, the double-helix carbon nanocoils with a coil diameter of about 500 nm were observed. As it is shown in Fig. 8, there are two patterns, in pattern A, two fibers twisted tightly without a coil gap to form the double-helix carbon nanocoils, similar to that mentioned by Baker [10]; in Pattern B, it is very unusual that the two fibers (width of 100 nm) cohere together to become a wide (width 200 nm) twin-fiber and a coil gap is about 100 nm. When using a Fe-Ni-Cr alloy at the same gas conditions, carbon coils of Patter B were also obtained, as it can be seen more clearly in Fig. 9.

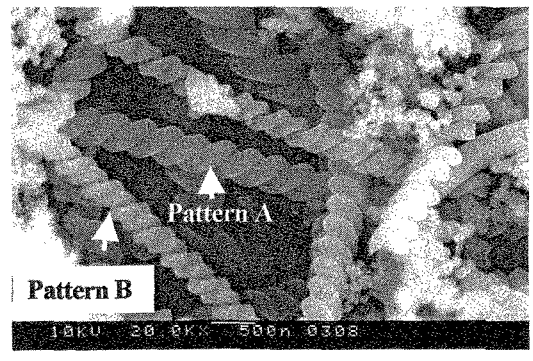

Fig. 8 As-grown double-helix carbon nanocoils over an alloy catalyst Fe-Cr-Mo-Sn, Pattern A & Pattern B co-existing.

3.3 Single-helix spring-like carbon nanocoils

The stainless-like plates were coated with Au and used as

the catalyst, kept other reaction conditions the same with previous section. Using this catalyst, spring-like single-helix coils with big pitch were formed. In some of the carbon coils, the fibers were trimmed with beautiful lace as shown in Fig. 10a.

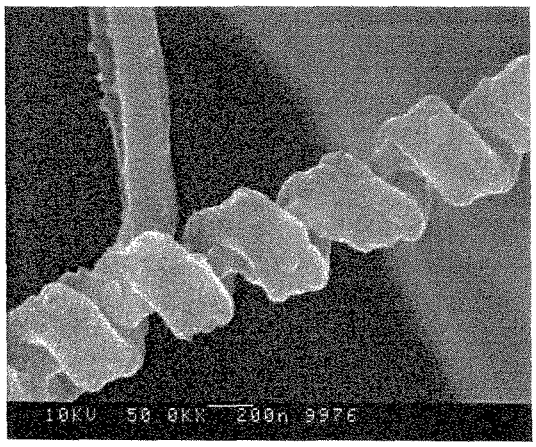

Fig. 9 Double-helix carbon nanocoils: Pattern B, grown over a Fe-Ni-Cr alloy.

By using WS_2 as the catalyst and controlling reaction conditions well, many nanostructures such as single-helix carbon nanocoils whose coil gap has the same size with the coil diameter (Fig.10b). In addition to single-helix coils, double-helix carbon microcoils and ribbon-like double carbon nanocoils with zero coil gap can be also obtained by WS_2 powder catalyst.

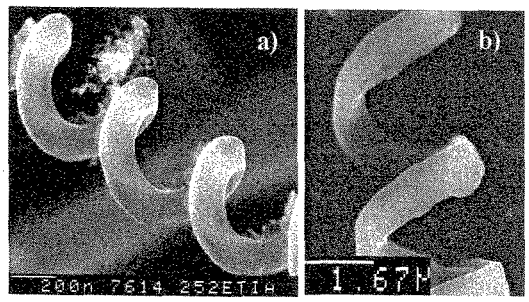

Fig. 10 Single-helix spring-like carbon coils grown over **a):** Au-coating stainless plate, **b):** WS_2 catalyst.

3.4 Proposed growth mechanism

Baker and co-worker [19] has observed helical carbon fibers during their studied on interaction of iron-nickel with ethylene-carbon monoxide- hydrogen mixtures at 600 ℃. However, in our system, to obtain large amount of the nanocoils, it is necessary to feed sulfur and keep the temperature between 650~800 ℃. It is reasonably to consider that the carbon nanocoils are also formed by the VLS mechanism, and the coiling driving force is the anisotropy of the catalyst grains on the growth tip under the presence of sulfur, just similar to carbon microcoils. However, because the conformation and chirality are different, there must be some difference in the composition in the qausi-liquid periphery and in the bulk crystal structure.

Finally, because of the spring-like form with big pitch the single-helix carbon nanocoils are expected to be used in microsensors and actuators, esp. in mechanical-electrical energy transfer nanomachines.

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