Transactions of the Materials Research Society of Japan 29 [2] 457-460 (2004)

Preparation and properties of super-elastic carbon microcoils by Ni-catalyzed CVD

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By Ni-catalyzed pyrolysis of acetylene at 700–850°C, carbon micro-coils (CMC) of double helical/spiral form were obtained. The influences of the reaction conditions on the morphologies and elasticities were examined. Circular coils with a circular fiber cross-section and large coil diameter of several dozen micrometers, those coils could be elastically extended up to 15 times of the original coil length (refer to as "super-elastic CMC"), were obtained. It was found that the reaction conditions were strongly affected the morphologies, microstructure and elasticities. The extension characteristics of the super-elastic CMC were investigated in detail. The CMC have high elasticities and high electromechanical properties, and are expected to have potential applications in microelectromechanical (MEMS) system.

Key words: Carbon microcoil, super-elasticity, Ni catalyst, acetylene pyrolysis

1. INTRODUCTION

Some researchers have occasionally observed the growth of helical/spiral carbon filaments during the vapor phase preparation of the carbon fibers [1-4]. However, their observation of helical/spiral filaments was extremely accidental, and there are neither reports on the control of coiling patterns and coil dimensions, nor on extension characteristics of the large amount of super-elastic coils by other researchers. We have reported the large scale preparation, morphology, growth mechanism of well-formed carbon micocoils (CMC), whose coiling diameter was about 5 microns and the coil gap is almost zero, by Ni-catalyzed CVD using acetylene [5-8]. We also once reported the growth of superelastic CMC [9].

Because of their special micro-helical, coiling- chiral morphologies and special properties such as coiling-chirality, high elasticity, low electrical resistance, and high specific surface area, that is, the combinations of a serious of outstanding properties carbon coils is a kind of potential candidate for novel functional materials such as electromagnetic wave absorbers, field emitting materials, hydrogen storage materials, tunable micro-devices, micro-sensors, micro-actuators, especially in microelectromechanica (MEMS) system , electrode materials, chiral catalyst, etc. By adjusting the coiling dimensions such as coiling diameters and coiling pitches, the CMC can become very elastic, that is, become micro/nano- srpings.

In this study, we prepared the super-elastic carbon coils with very high elasticity by the Ni-catalyzed pyrolysis of acetylene containing a small amount of sulfur compound as an impurity. The preparation conditions, morphology, microstructure and mechanical properties of the super-elastic CMC were examined in detail.

2. EXPERIMENTAL

CMC were prepared by the Ni catalyzed pyrolysis of acetylene at 700-800°C for 2 h. Horizontal reaction tubes (quartz, 55 mm i.d.) using graphite plate as the substrate, on which Ni powder catalyst (5 μm diam.) was dispensed, were used. The source gases (acetylene+H_2+N_2+sulfur impurity) were vertically introduced onto the substrate surface.

3. RESULTS AND DISCUSSION

3.1 Morphology of regular carbon coils

The carbon microcoils (CMC) grew uniformly on the surface of the substrate. The thickness of coil layers was 2–3 mm after a 2 h reaction time.. The regular-coiled carbon fibers (referred to as " regular CMC" hereafter) with a constant coil diameter and coil pitch throughout a piece of the carbon coils could be obtained under the following reaction conditions (referred to as "standard reaction conditions" hereafter): reaction temperature 760–790°C, reaction time 2 h, acetylene flow rate 60 sccm (ml/min), thiophene gas flow rate 2.5–5 sccm. The regular CMC generally grew vertically on the substrate surface pointing the coil tip to the source gas inlet direction. The representative morphology of the regular CMC is shown in Fig. 1. The regular CMC were usually composed of two double-helical regular-coiled carbon fibers with flat or rectangular-form in fiber cross-section and without the coil gap between adjacent two carbon fibers. The coil diameter was generally 5–8 μm and coil length was 3–6 mm. The as-grown CMC can be extended elastically to 1.3–2 times the original coil length such as shown in Fig. 2.

3.2 Morphology and extension characteristics of representative super-elastic CMC

The super-elastic CMC grew in a relatively small amount of acetylene and total gas flow rates than the

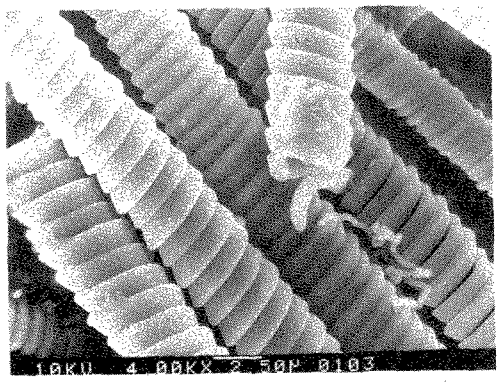

Fig. 1. Regular carbon microcoils without a coil gap.

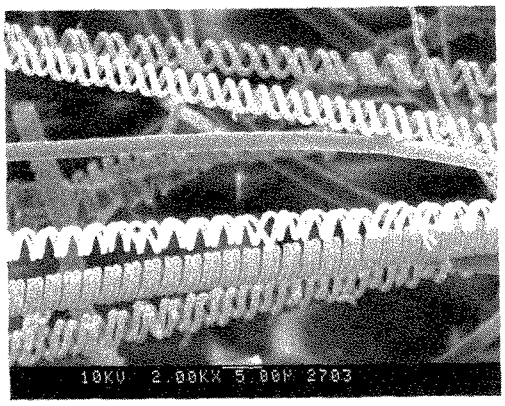

Fig. 2. Extensive state of the regular carbon microcoils.

"standard reaction conditions". They were generally irregular-coiled CMC with the fibers in relatively circular cross-section and a larger coil diameter of 10–20 μm as shown in Fig. 3, while that of the regular CMC is 3–6 μm. Furthermore, the super-elastic CMC have a larger coil gap of 0.2–2.0 μm, while the regular CMC have no coil gap. The super-elastic CMC have commonly the same double helical forms as those of regular CMC.

The growth tip of a super-elastic CMC and its enlarged view are shown in Fig. 4, in which an Ni catalyst grain can be seen (Fig. 4b, arrow). It indicates that the deposition forms of carbon from an Ni catalyst grain are irregular and the deposited carbon fibers are not sufficiently curled near the catalyst grain, while that of regular CMC are curled enough to form regular and small coil diameter.

Fig. 5a shows the extension characteristics of the as-grown and bulk (blanket-like) super-elastic CMC. Fig. 5b shows the enlarged view, comparing with Fig. 2, the bulk CMC are extended to more than 5 times of the original coil length. The CMC could expand to linear form with increasing applied load, and double coil forms are maintained. For example, coil A was extended to a straight form, coil B was bigger than coil C. The CMC extended to far from a straight form could recover the original coil length after releasing the extension force while the CMC that extends to a straight form could not recover the original coil length.

Fig. 3. As-grown super-elastic carbon microcoils.

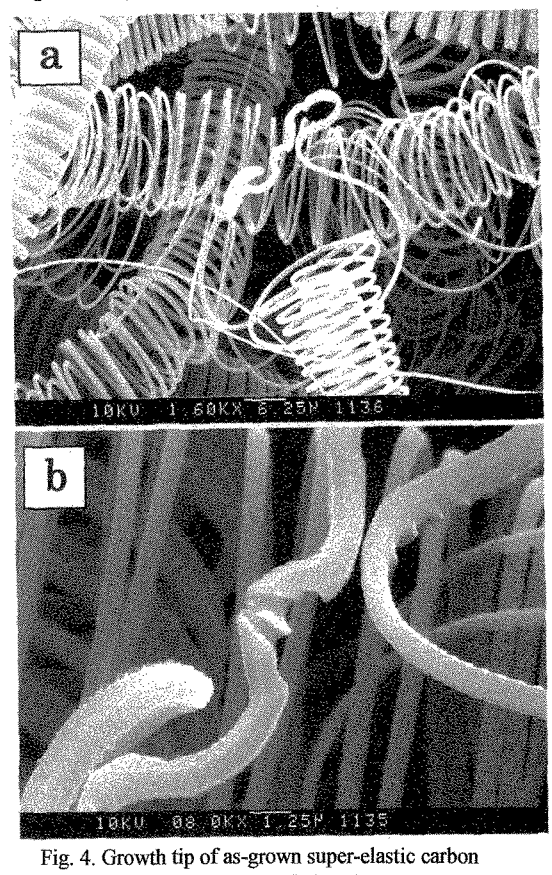

Fig. 4. Growth tip of as-grown super-elastic carbon microcoil (a) and the enlarged view (b).

3.3 The influences of gas flow rate conditions on the morphology of the super-elastic CMC

As is shown in Fig. 6, by much lower total gas flow rates, the coil diameter increased further, reached to as large as 50 μm and the coil pitch as big as 5 μm at the expense of low coil yield, On two sides of the substrates, where the gas concentrations were more dilute, thus the coils diameter might become too big that lost their regularity fully and look like straight fibers (not fully straight but curling). On the other hand, comparing Fig. 7 with those of representative elastic coils shown in Fig. 3, when increased hydrogen flow rates only, the coil pitches

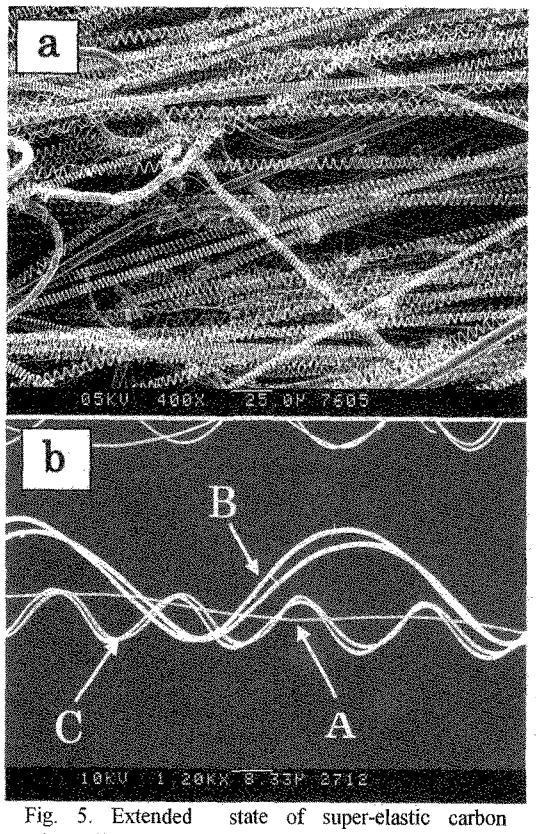

Fig. 5. Extended state of super-elastic carbon microcoils (a) and the enlarged view (b).

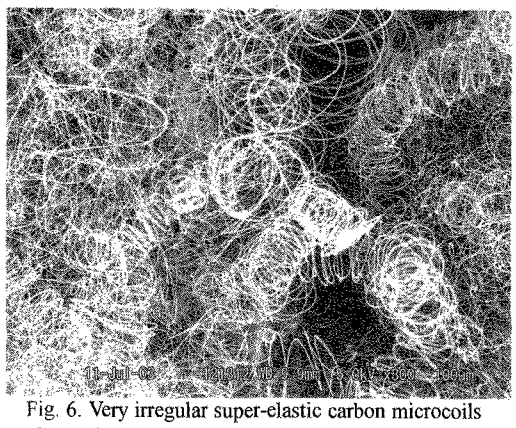

Fig. 6. Very irregular super-elastic carbon microcoils obtained by more lower gas flow rates.

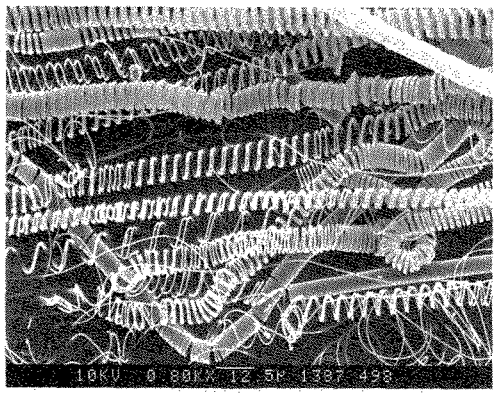

Fig. 7. Super-elastic carbon microcoils obtained by high H_2 flow rate.

were increased to 5 μm, while coil diameters were not increased obviously, remained about 15 μm. Thus, it can be concluded that by adjusting gas flow rates only, coil diameters and coil pitches can be prepared controllably.

3.4 The influences of other reaction conditions on the morphology of the super-elastic carbon coils

By changing a serious of preparation process, some interesting coiling morphologies could be obtained. For example, start the reaction in the standard conditions, allowing to react for 0.5 h, then stop the reaction, allow the reaction tube to be cooled down, then re-started the reaction again, at the same conditions, elastic CMC with a coil diameter of 2.5 μm, and a coil pitch of almost the same, as shown in Fig. 8, but the coil yield remain to be

Fig. 8. Super-elastic carbon microcoils obtained by stopping and re-starting at 770℃.

improved. When using Ni powder catalyst which was oxidized in air at about 700 ℃ for 30 min, and then start the CVD process for the growth of the CMC, we obtained smaller CMC with small coil diameters of about 1~2 μm, a coil pitch of about the same order of the diameter (Fig. 9). We still do not know the mechanism of the dependence of these coils on the reaction conditions, further investigation is needed.

3.5 The microstructure and the heat-treatment behavior of the super-elastic CMC

The sample was heat-treated at 2500℃ for 0.5 h, and the obtained bulk CMC and the coil tip are shown in Fig. 10. The growth of graphite layers can be seen, while the coiling pattern remained undestroyed. Near the growth tip, the coil are full of holes, may be due to some chemical components, such as hydrogen, got out from the coils. Fig.11 shows the extended state of the heat-treated CMC at 2500℃ for 0.5 h, indicating that the heat-treated (graphitized) CMC were remained their elasticity to some extent.

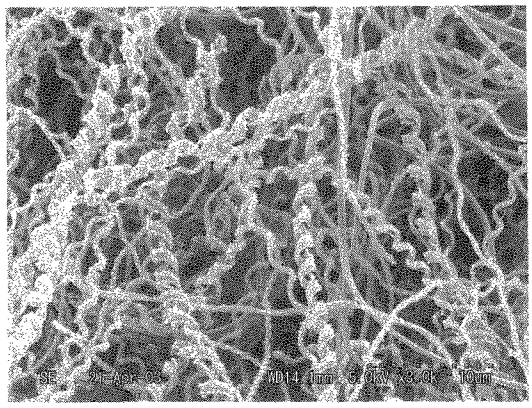

Fig. 9 Super elastic coils obtained by oxidized Ni.

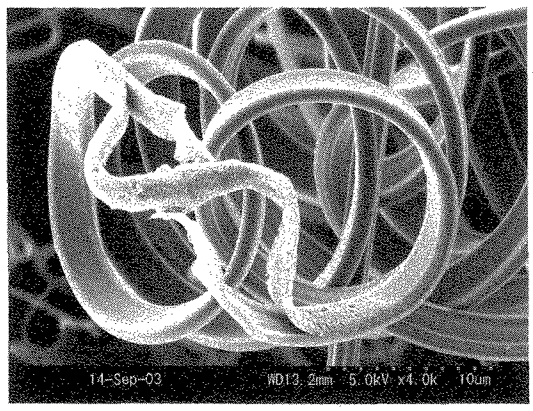

Fig. 10. A grow tip of the heat-treated superelastic carbon microcoils.

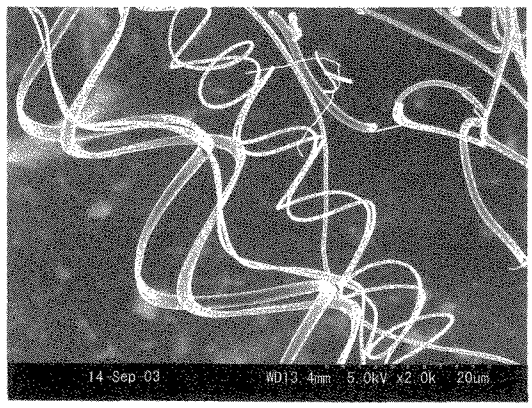

Fig. 11. Extensive state of the heat-treated superelastic carbon microcoils.

3.6 Potential applications of the super-elastic CMC

The superelastic CMC could be extended up to about 5 times original coil length and maintained the electrical conductivity as shown already. It is expected that composite of the superelastic CMC and elastic polymers show changing in electrical properties such as inductance (L), capacitance (C), resistance (R), when applying loads, such as pressing, picking, brashing, etc. Accordingly, the superelastic

CMC can be used as sensors, microelectromechanical system (MEMS), electromagnetic absorbers, high-conducting materials with superelasticity, etc.

4. CONCLUSIONS

By Ni-catalyzed pyrolysis of acetylene at 700–850°C, carbon micro-coils (CMC) of double helical/spiral form with super–elasticity were obtained. The ratio of a coil pitch against a coil diameter could be controlled by adjusting the reaction conditions. The Circular fiber CMC with circular fiber cross-section and with a large coil diameter of several dozen micrometers, those CMC could be elastically extended up to more than 5 times of the original coil length, were obtained. After high temperature-treated at 2500 ℃, graphite structure was formed in some degree, but the coils (graphite coils) remained their elasticities in some extent. The carbon coils with a large ratio of coil pitch against coil diameter ($R_{P/D}$) have high elastic property and thus high microelectromechanical properties as well as more excellent EM wave ability than that of regular CMC can be expected.

Acknowledgement

This work was supported by the Innovative Technology (No.13506) and a Aid for Scientific Research (No. 13555171) from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and JSPS (P02372).

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(Received October 11, 2003, Accepted December 15, 2003)