Transactions of the Materials Research Society of Japan 29 [2] 485-488 (2004)

Preparation and morphologies of elastic carbon microcoils/nanocoils by various catalysts

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Carbon microcoils (CMC) with double helical/spiral forms or single-helix form, coil diameter in micron order or nanometer order and with large coil pitches, thus with high elastic properties were obtained by the catalyzed pyrolysis of acetylene at 700–850°C using Ni/Fe-base alloys, W/WS_2 as the catalysts. The preparation conditions, morphology, and extension characteristics were examined, and the influences of the metal catalyst on the elasticity are discussed.

Key words: carbon microcoil, carbon nanocoil, elasticity, catalyst.

1. INTRODUCTION

Fibrous carbon nanostructures such as carbon nanotubes (CNT)[1] and carbon nanofibers (CNF) [2-5] have intriguing properties [6-7]. There are several methods to synthesize CNFs, for example arc discharge, laser vaporization, and chemical vapor deposition (CVD). Among them, CVD is an effective method for direct growth of CNFs on certain substrates at relatively low temperatures. In addition to the purity of the product, the CVD method allows the growth of large amounts of CNFs at lower cost because it proceeds at moderate temperatures (below 1273 K). Moreover, the control of nanofiber structure can be realized by regulating the reaction parameters and catalyst composition as well as by modifying the nanomorphologies of the catalysts with dispersion of metals on supports. Although pure transition metals such as Fe, Ni, and Pd are commonly used as the catalysts for CNT and CNF formation, it was reported that alloy catalysts are effective for low temperature growth of CNTs and CNFs.

The syntheses of CNTs or CNFs in CVD process runs by a non-well-defined-mechanism. A first step is assumed where the carbon source is decomposed on the active points of the catalyst, and gives carbon atoms with concomitant desorption of molecular hydrogen. Carbon is then supposed to dissolve in and diffuse through the bulk of the metal, yielding finally carbon nanofibers and the metal. This general mechanism was already proposed for carbon nanofibers by Baker et al [8] in the 1970s and it has been widely accepted. The inverse dependence of growth rate on particle width also proposed by Baker, and is consistent with a diffusion-controlled mechanism. The latter authors admit the formation of carbide intermediate species to explain the thermodynamics of diffusion in the last mechanism. These carbides would decompose in carbon nanofibers and the metal [4]. Although the formation of these carbide intermediates species is still in doubt because it is difficult to demonstrate since they constitute an intermediate species.

We have prepared the carbon microcoils or nanocoils having a micro-ordered or nanometer-ordered coil diameter (referred to as 'carbon micro coils (CMC)' hereafter) with good reproducibility by the catalytic pyrolysis of acetylene containing a small amount of sulfur impurity, and reported the preparation conditions, morphologies, and some properties in detail [9-22]. Recently, we have found that carbon nanocoils with different coiling patterns can be obtained by acetylene CVD over Fe-containing alloy catalysts. In this study, spring-shape or wave–shape elastic carbon micro/nano-coils were synthesized by the catalytic decomposition of acetylene, over Ni-Fe alloys catalysts, and WS_2 catalyst. Our objective was to test various kinds of catalysts to obtain elastic carbon coils with different coiling patterns and dimensions.

2. EXPERIMENTAL

Acetone-dissolved commercial acetylene was used as the carbon source without further purification. Ni, Fe-base alloys of Fe-Cr-Ni , Fe-Ni-Co, Fe-Cr-Ni-Mo, Fe-Cr, W+WS_2, and WS_2 powder (5 μm average diameter) were used as the catalysts, these catalyst powders were dispensed on the surface of the substrate that was placed in the central part of the reaction tube (quartz, 30 mm i.d.). A small amount of thiophene was used as the promoter for the growth of the carbon coils. A gas mixture of acetylene 50~100 sccm (ml/min), sulfur compounds 0.1~15 sccm, hydrogen 100~200sccm, and nitrogen 50~200 sccm was introduced into the reaction tube which was heated at 650~800 °C from the outside using an AC electric heater.

3. RESULTS AND DISCUSSION

3.1 Morphology of regular CMC grown over Ni powder catalyst

The regular-coiled carbon fibers with a constant coil diameter and coil pitch throughout a piece of the carbon coil (referred to as " regular carbon microcoil or regular CMC" hereafter) could be obtained under the following reaction conditions (referred to as "standard reaction conditions" hereafter): reaction temperature 770–780°C, reaction time 2 h, acetylene flow rate 60 sccm, thiophene content in total gases 2.5–20 sccm. The regular CMC grew generally pointing to the source gas inlet direction on the substrate surface. The representative morphology of the regular CMC is shown in Fig. 1. The CMC is usually composed of two double-helically and regularly-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 up to 1.3–2 times the original coil length.

3.2 Morphology of elastic carbon microcoils prepared by various catalysts

3.2.1 Super-elastic CMC with double-helical forms grown over Ni powder

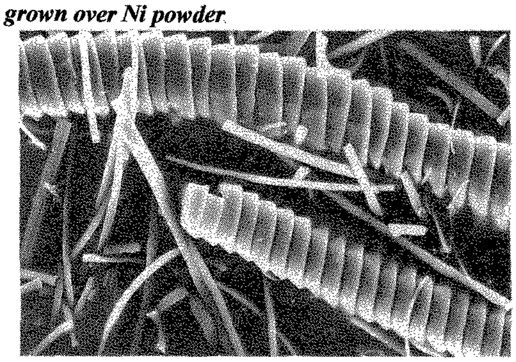

Fig.1. Regular carbon microcoils. Reaction temperature: 760°C, catalyst: Ni powder.

The super-elastic CMC with super elasticity were obtained in a relatively small amount of acetylene and total gas flow rates than the "standard reaction conditions" at which very regular carbon coils could be obtained [22]. They were generally irregular-coiled CMC with a circular in fiber cross-section and a larger coil diameter of 10–50 μm than that of the regular CMC of 2–8 μm as shown in Fig.2. Furthermore, the super-elastic carbon coils have a larger coil gap of 0.2–5.0 μm while the regular carbon coils have no coil gap. The super-elastic carbon coils commonly have double-helical forms the same as those of regular carbon coils. It is considered that reducing acetylene and/or total flow rates may result in the decrease of the anisotropic composition on the respective Ni catalyst crystal faces and thus the decrease of the anisotropic carbon deposition to form larger coil diameter and coil pitch. If there is no anisotropy between the respective crystal faces, then a straight carbon fiber will be formed [13, 16, 22].

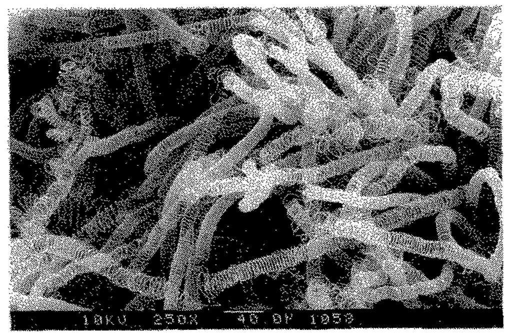

Fig. 2. Super-elastic irregular carbon coils with circular fiber cross-section and large coil diameter. Reaction temperature: 760°C, catalyst: Ni powder.

3.2.2 Single-helix CMC carbon grown over Fe-group alloys

Fig.3 shows the CMC with large coil pitches obtained using a Fe54-Ni29-Co17 alloy catalyst. It can be seen that the CMC have single-helix form, however, their coil diameters and coil pitches are not uniform. There are three kinds of representative helical patterns, the biggest is shown by a circle, its coil diameter is 1.5 μm, its coil gap is 3 μm, the ratio of the coil diameter against the gap $R_{D/G}$ is about 0.5; the second is shown by a rectangular, its diameter is about 0.5 μm, and coil gaps about 1 μm, $R_{D/G}$ is also about 0.5; the third one is shown by a triangular, it is of spring-like form, coil diameter and coil gap are about 0.5 μm, the ratio of the coil gap against the diameter D/G is about 1. It is clear that the coiling patterns of these fibers are quite different from those shown in Figs.1 and 2. It is well known that catalyst composition is an important factor. Comparing with these coils with those shown in Figs. 1~2, it was found that by adding Fe and/or Co element into Ni catalyst, The CMC with large coil pitch is formed.

It is found that the additions of the different metals such as Sn, Cr or Mo, Mn could promote the growth rate of these coils or adjust their helical forms. This observation agrees with the results obtained by other researchers [5]. Fig. 4 shows that the regular single-helix CMC grown over Fe-Ni-Cr alloy, which have a coil diameter of about 4 um, coil gap of about 2 μm, and $R_{D/G}$ about 2. Fig. 5 shows another interesting CMC formed over the same catalyst.

There are two kinds of coiling patterns, in the first pattern, three fibers coalescenced together and coiled in a diameter of about 500 nm, while in the second coiling pattern, the single fiber curled in "S" shape. It is also found that Ni is important for producing CMC in high yield. For example, in Fig. 6, the CMC were grown over Fe74-Cr26 (without Ni), the diameters and the coil gaps distributionis similar to that of Fig.3, but the yield was lower.

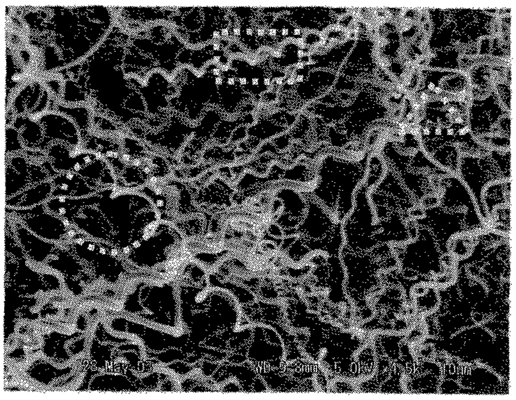

Fig. 3. Single-helix carbon coils with large coil pitches. Reaction temperature: 760°C, catalyst: Fe54-Ni29-Co17.

3.2.3. Single-helix CMC grown over tungsten and its compounds

Tungsten is also a mystery metal for the growth of the CMC, and uptill now, double-helical CMC, ribbon-like coiled CMC, and single-helical CMC with different coil diameter and coil pitches were obtained. Fig. 7 shows the CMC obtained using WS_2 as the catalysts at 740 ℃. The outer diameter is several microns or several hundred nanometers, the coil pitch is about the same size with the coil diameter, and the length is 0.5 mm. The optimum catalysts for obtaining double-helix super-elastic CMC such as shown in Fig. 8 were $W+WS_2$, in this case the main component act as the catalyst may be W, similar to pure metal Ni.

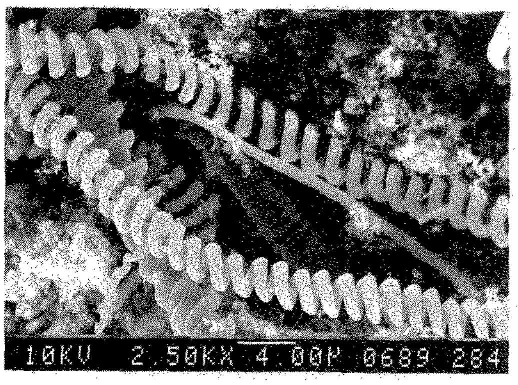

Fig. 4. Regular single-helix carbon nanocoils. Catalyst: Fe-Cr- Ni.

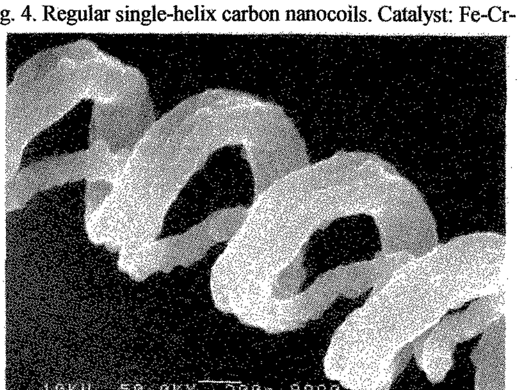

Fig. 5. An interesting carbon nanocoil.Catalyst: Fe-Cr- Ni.

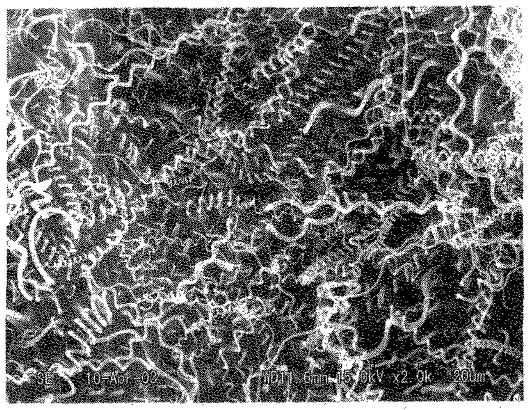

Fig. 6. Carbon coils with large coil pitches. Reaction temperature: 600℃, catalyst: Fe74-Cr26.

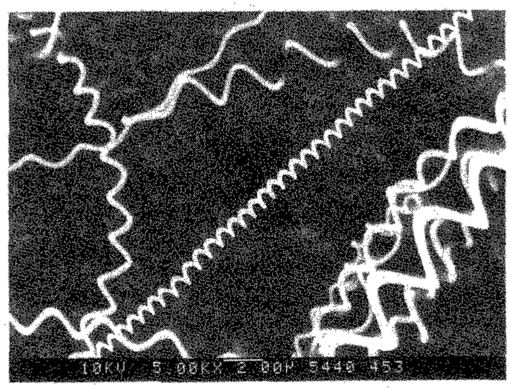

Fig. 7. Carbon coils with large coil pitches, Reaction temperature: 760°C, by WS_2.

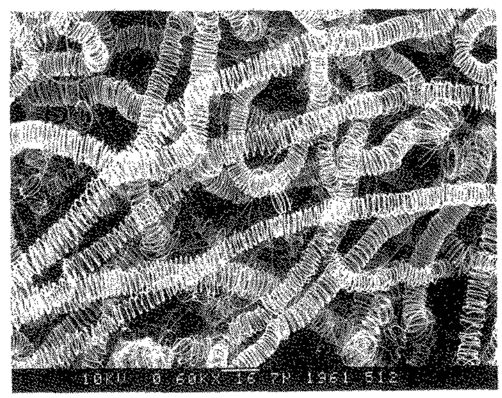

Fig. 8. Carbon microcoils with large coil diameter. Reaction temperature: 750°C, by $W+WS_2$ catalyst.

3.3. Extension characteristics

Fig. 9 shows the extension characteristics of the bulk (blanket-like) CMC. The bulk CMC are extended to about 5 times of the original length. The CMC could be extended linearly with increasing applied load. It was found that some CMC are extended to nearly straight forms, in which double coil forms are maintained. The extended CMC could recover the original coil length after releasing the extension force as shown in Fig. 10.

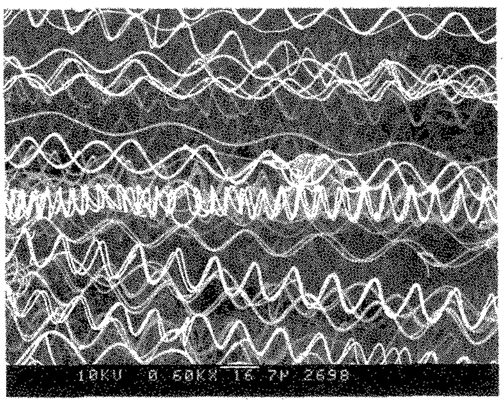

Fig.9. Extension characteristics of carbon microcoils with big coil diameters.

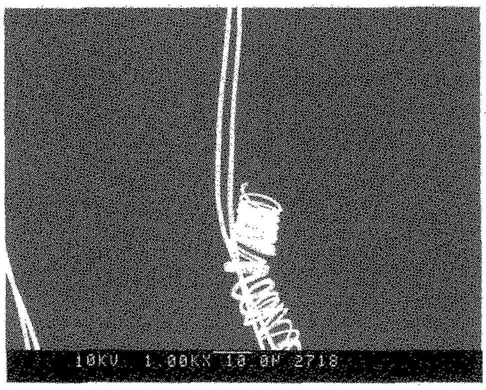

Fig. 10. Extension characteristics of carbon microcoils with big coil diameter: recovery state after releasing the extension.

4. CONCLUSIONS

Carbon coils with double helical/spiral forms or single-helix form, coil diameters in micron order or nanometer order and large coil pitches, thus with high elastic properties were obtained by the catalyzed pyrolysis of acetylene at 700–850°C using Ni, various Fe-base alloys, WS_2, and $W+WS_2$ catalysts. Using Ni catalysts, at low gas fowl rates than those for regular CMC, the CMC with coil diameters range from 10 to 50 μm, coil pitches range from 0.5 to 5 μm, and with super-elastic extension property can be obtained with good reproducibility and purity; Using various Fe-base alloys as the catalyst, the CMC with the ratio of pitch against diameter range in 1~3 μm can be obtained. Using WS_2 and WS_2+W, both these two kinds of elastic CMC could be obtained.

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, as well as JSPS (P02372).

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