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Vapor Phase Preparation of Cosmo-mimetic Carbon Micro-coils and Their Properties

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Cosmo-mimetic carbon micro-coils were prepared by the metal catalyzed pyrolysis of acetylene at 750-800℃. The preparation conditions, morphology, growth mechanism, and some properties of the carbon coils were examined. The carbon coils have an amorphous phase with a double helix structure similar to DNA, and have a coil diameter of 1-10 μm and coil pitch of 0.1-1 μm. The coil length increased with increasing reaction time and was about 20 mm long after a 10-hr reaction time. The coil yield increased by appling DC or AC bias voltage, except for the Ta. The super-elastic carbon coils, which could be linearly expanded with an increasing appling load up to 10-15 times that of the initial coil length were obtained. The amorphous carbon coils could be graphitized with full preservation of the coiling morphology by heat-treatment up to 3000℃.

" Key words" chemical vapor deposition (CVD), vapor grown carbon fibers (VGCF), acetylene, helical-form, catalyst.

1. Introduction

Materials with various morphologies such as bulk, thin film, powder, straight fiber or whisker are commercially available. However, materials with 2D or 3D-helical/coiled fibers have never been available while these are expected to having novel applications as tunable microdevices/sensors, electromagnetic absorbers, hydrogen absorber, chiral catalysts, etc. The vapor growth of various micro-coiled fibers such as SiC(1-3), Si3N4(4-7), BN(8), and B(9) have been reported. Furthermore, vapor growth of the micro-coiled carbon fibers or nanotubes has also been recently reported (10-12). However, the growth of these coiled fibers is mostly accidental and the reproducibility is very poor. We have prepared the cosmo-mimetic carbon micro-coils (referred to as "carbon coils" hereafter) with high reproducibility by the catalytic pyrolysis of acetylene, and reported on the preparation conditions, morphology, growth mechanism and some properties (13-16).

In this study, we examined the effect of the preparation conditions on the growth of the long and super-elastic carbon coils and also determined some of their properties.

2. Experimental

The carbon coils were prepared by the Ni-catalyzed pyrolysis of acetylene at 750-800℃ for 2 hrs. The reaction apparatus used for the growth of the long carbon coils is shown in Fig. 1. The source gas mixture of C2H2+H2+N2+thiophene was vertically introduced on the substrate surface on which Ni powder was dispersed. The detailed preparation conditions are shown in ref. 17.

3. Results and Discussion

3.1. Preparation of long carbon coils:

During growing of the carbon coils, the carbon coil layersgrew to the source gas inlets resulting in the reduction of the temperature and growth rate. Accordingly, the separation of the tip part of carbon coil layers and the source gas inlets was controlled to maintain within 5 mm during the reaction. Fig. 2 shows the coil layers grown on the graphite substrate. It can be seen that the average thickness of the coil layers reached 15 mm high. Fig. 3 shows the effect of the reaction time on the average thickness of the coil layers in relation to the kind of substrates. The thickness of coil layers increased with increasing reaction time up to about 6 hrs and then the growth rate was reduced to attain a constant length depending on the substrate. The average thickness of 18-20 mm was obtained using a Ni, W or Nb substrate.

3.2. Effect of bias voltage on the growth of the carbon coils:

It is well known that the application of a vias voltage on a reaction atmosphere or substrate accelerates the chemical reaction, nucleation and thus growth of the crystals or fibers(18-19). We found that a bias voltage applied to the graphite substrate accelerates the growth of the carbon coils by the Ni-catalyzed pyrolysis of acetylene (20). Fig. 4 shows the effect of a DC bias on the yield of the carbon coils obtained with Nb and Ta as the catalyst A negative or no effect of the DC bias voltage was observed for a Nb and Ta catalyst while a strong positive effect was observed for the Ni catalyst. On the othe rhand, the DC bias increased the coil yieldwith a Ni and Nb catalyst while it decreased with Ta as shown in Fig. 5. The magnetic properties of these metals at high temperatures are not known. However, The observed bias effects on the growth of the carbon coils may have some correlations with the Nb and Ta metals as they are paramagnetic while Ni is ferromagnetic at room temperature.

3.3. Morphology:

Figs. 6 and 7 shows the representative regular and irregular carbon coils obtained using a Nb catalyst, respectively. The tip part of the carbon coils have usually rewound-like forms resulting in irregular coiling forms, and also have a catalyst grain on the central part of the tip as shown in Fig. 7.

3.4. Super-elastic carbon coils:

The regular carbon coils with a flat or rectangular cross section and irregular carbon coils with a circular or eliptical cross section could be elastically expanded up to about 1.5 times (17) and 4.5 times (21), respectively. We have found that regular carbon coils with circular or eliptical cross section could be expanded to about 10-15 times that of the original coil length. Fig. 8 shows the carbon coils elastically expanded to nearly a straight form.

3.5. Heat-treatment:

Based on x-ray diffraction (XRD), Raman spectra and electron diffraction pattern, it was found that the as-grown carbon coils have an almost amorphous phase. The as-grown carbon coils were heat-reated under an Ar atmosphere at 1300℃ for 5 hrs. The XRD pattern of the heat-treated carbon coils is shown in Fig. 10. It can be seen that the amorphous carbon coils were slightly graphitized by the heat treatment at 1300℃. TEM image and electron diffraction pattern of the heat-treated carbon coils are shown in Fig. 11. The ruptured cross section of the heat-treated carbon coils were slightly pyramidal on one side and hollow on the other while that of the as-grown carbon coils was almost flat. It can be seen in Fig. 11(b) that anisotropic Debye-Sherrer rings can be seen, suggesting the formation of anisotropic graphite layers by the heat treatment.

3.6. Growth mechanim:

It is considered that the carbon coils grew by the anisotropic mechanism of the catalyst grain (22-23). However, the growth mechanism of the flat or rectangular carbon coils is not well known yet. Fig. 12 shows the carbon coils heat-treated up to 1400℃ at the increasing rate of 10℃/min by a TG. It can be seen that four edge parts of the rectangular carbon coils were preferentially etched out to form four graphite parts, probably caused by the oxidation of the contaminant oxygen present in the heat-treatment atmosphere. That is, this result shows that the carbon coils are composed of four parts of the carbon deposits extruded from the crystal faces of a catalyst grain. A model for the growth mechanism can be deduced from these results. In this model, a catalyst grain have an elongated octagonal form as shown in Fig. 13, and the coiling patterns can be formed by the catalytic anisotropy between the four crystal faces (A-D).

4. Conclusions

Carbon micro-coils with micron-ordered coil diameters were prepared by the metal catalyzed pyrolysis of acetylene at 750-800℃. The preparation conditions, morphology, growth mechanism, and some properties of the carbon coils were examined. The carbon coils with an 18-20 mm coil length were obtained after 6 hrs by controlling the separation between the coil layers and gas inlets. The super-elastic regular carbon coils with the expantion ratio of 10-15 times that of an original length was obtained The coil yield increased by applying a DC or AC bias voltage except for Ta. The amorphous as-grown carbon coils could be graphitized with full preservation of the coiling morphology by the heat-treatment.

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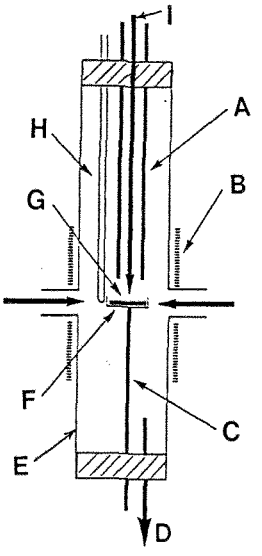

Fig. 1. Apparatus used for the preparation of the long carbon coils. A) source gas inlet, B) heater, C) support, D) gas outlets, E) reaction time, F) susceptor, G) substrate, H) CA thermocouple, I) source gas inlets. (C_2H_2+H_2+Ar+thiophene)

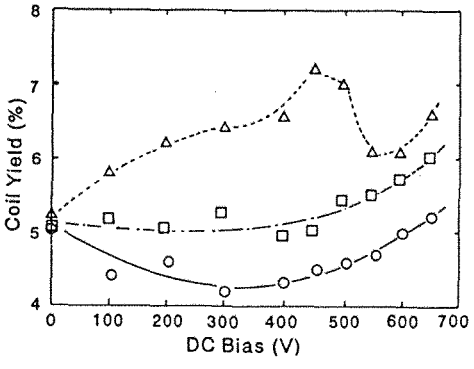

Fig. 4. Effect of DC bias voltage on the coil yield. Catalyst: (△) Ni, (□)Nb, (◯) Ta.

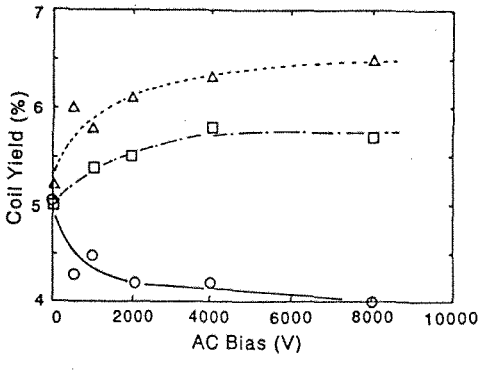

Fig. 5. Effect of AC bias voltage on the coil yield. Catalyst: (△) Ni, (□)Nb, (◯) Ta.

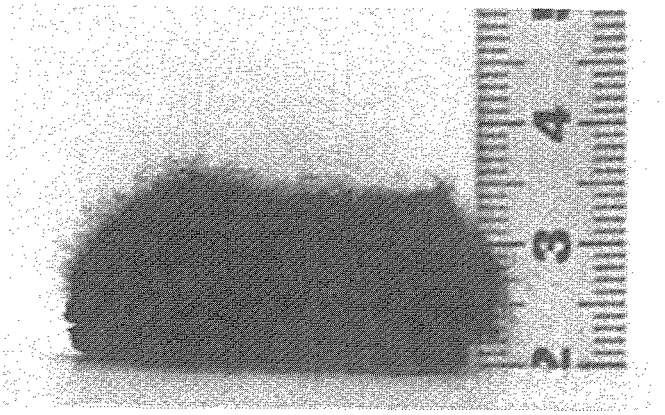

Fig. 2. Coil layers grown on the substrate.

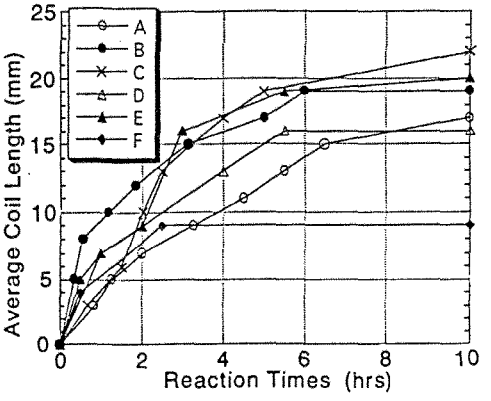

Fig. 3. Effect of reaction time on the thickness of the coil layers. Substrate: A) graphite, B) Ni, C) W, D) Ti, E) Nb, F) Co.

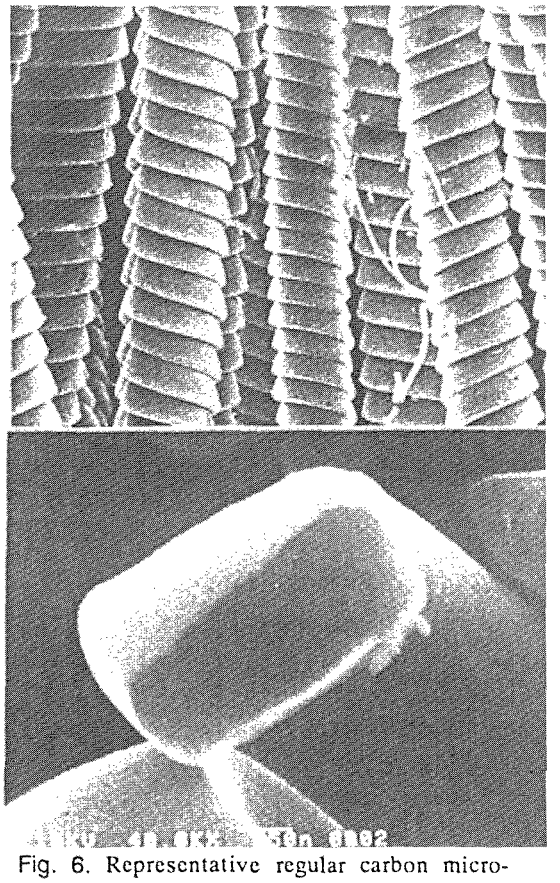

Fig. 6. Representative regular carbon micro-coils (a) and ruptured cross sectio (b).

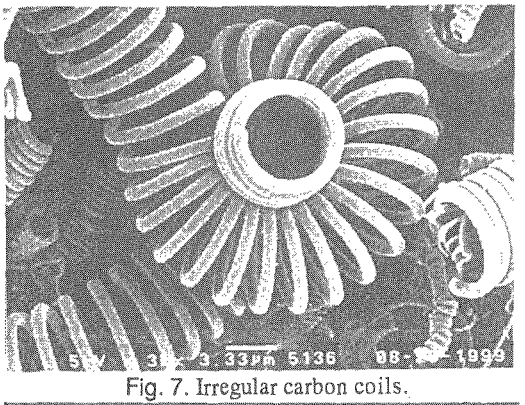

Fig. 7. Irregular carbon coils.

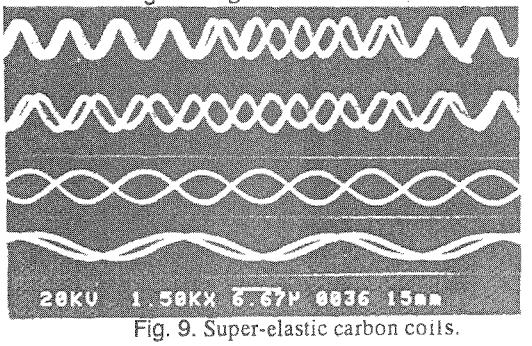

Fig. 9. Super-elastic carbon coils.

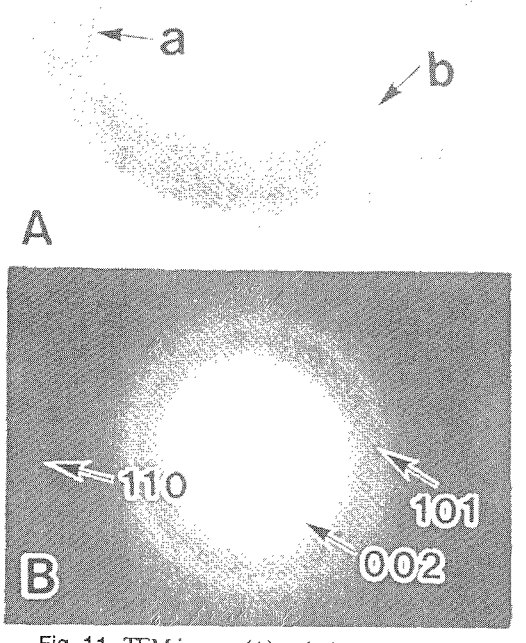

Fig. 11. TEM image (A) and electron diffraction pattern (B). a) hollow part, b) pyramidal part.

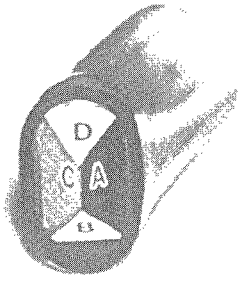

Fig. 13. Growth model of the carbon coils with a rectangular cross section.

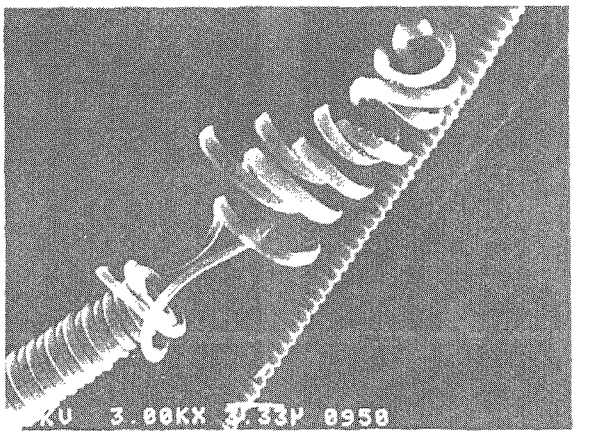

Fig. 8. Tip part of the carbon coils. Arrrow indicates a Ni catalyst grain.

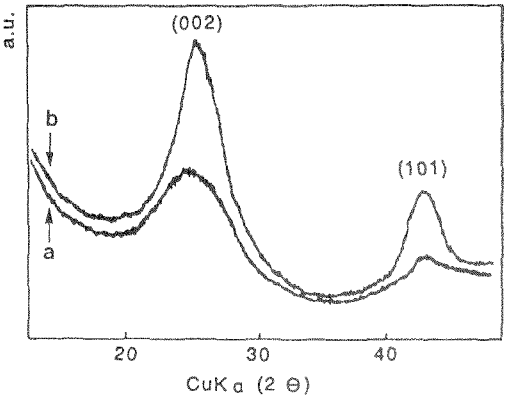

Fig. 10. XRD patterns. a) as-grown carbon coils, b) heat-treated carbon coils at 1300℃ in Ar.

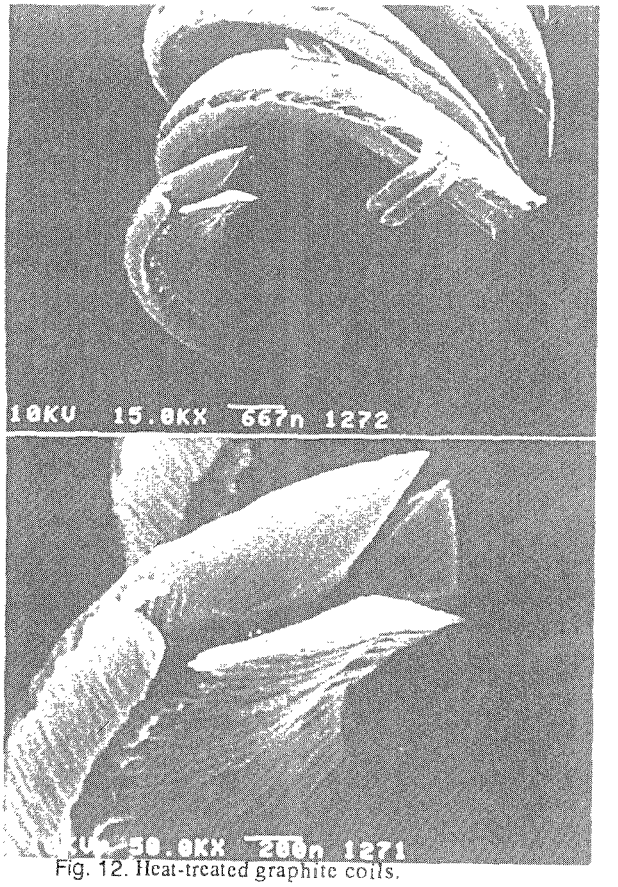

Fig. 12. Heat-treated graphite coils.