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# Preparation of carbon microcoils by catalytic methane hot-wire CVD process

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**Abstract**

Three-dimensional (3D) double-helix carbon microcoils (CMCs) were synthesized by the catalytic pyrolysis of methane using Ni catalyst in various hot-wire CVD processes. The most effective process is: using preheating method, in which methane was preheated at 1500 °C in a upper reaction tube by a hot wire, and chemical vapor deposition of carbon then occurred at 700–750 °C in a lower reaction tube, where CMCs were synthesized. The growth morphologies and microstructure were examined and compared with the conventional CMCs grown by acetylene catalytic pyrolysis.


*Keywords:* Carbon microcoil; Methane; Hot-wire CVD; Preparation; Morphology; SEM

## 1. Introduction

We have reported about regularly microcoiled carbon fibers (referred to as CMCs hereafter) synthesized in large scale with a high reproducibility by the catalytic pyrolysis of acetylene with a small amount of sulfur or phosphorus impurity, and about the preparation conditions, morphology, growth mechanism and some properties [1]. On the other hand, many carbon compounds other than acetylene [1], such as CO [2], propane [3], methane [4], ethylene, propylene, 1-butene, cis-2-butene, and 1,3-butadiene [5] were also used as the carbon sources for growing carbon fibers. Metal-catalyzed hydrocarbons usually decompose to form some amounts of acetylene, which are effectively available for growing carbon coils as already reported by us. However, when using hydrocarbons other than acetylene, the CMCs were rarely obtained under any reaction conditions. Among the hydrocarbons, methane is very advantageous against acetylene from a cost point of view because city gas mainly consists of methane. Accordingly, the use of methane as a carbon source for obtaining carbon coils has a large cost merit. Although methane was used to synthesized carbon nanotubes [6–8] and carbon nanofibers [9–11] by many researchers, there is no report on the preparation of CMCs using methane yet.

In this study, we prepared elastic CMCs by the Ni-catalyzed pyrolysis of methane which was preheated at high temperatures by a hot wire, and examined the effects of preheating conditions on the growth of the carbon coils and the morphologies. By this success in preparing elastic CMCs using methane, the cost can be reduced to about 50%.

## 2. Experimental

The schematic of three reactors used is shown in Fig. 1. In Reactor A, inside the vertical quartz reaction tubes (23 mm i.d. and 40 mm long), graphite substrate was set, a stainless rod around whom W filament was coiled, was set above the graphite substrate, Ni powder was sprayed on the graphite plate as the catalyst. $N_2$ was introduced first to drive out most of the oxygen. A tungsten (W) hot wire was heated to 1500–1900 °C under $N_2$ atmosphere, and when the temperature of the substrate reach to 820–850 °C, the reaction gases were introduced as shown in the Fig. 1A. In Reactor B, the locations of the W hot wire and the substrate were adjusted as shown in Fig. 1B.

On the other hand, Reactor C is an improved reactor based on reactor A and B; it composes of two reaction tubes, for preheating, and for CMC growing in CVD process, respectively. A horizontal quartz reaction tubes (23 mm i.d. and 40 mm long), was set upper, a stainless rod around whom W filament was coiled, was set through its axis. Another lower quartz reaction tube, which has a

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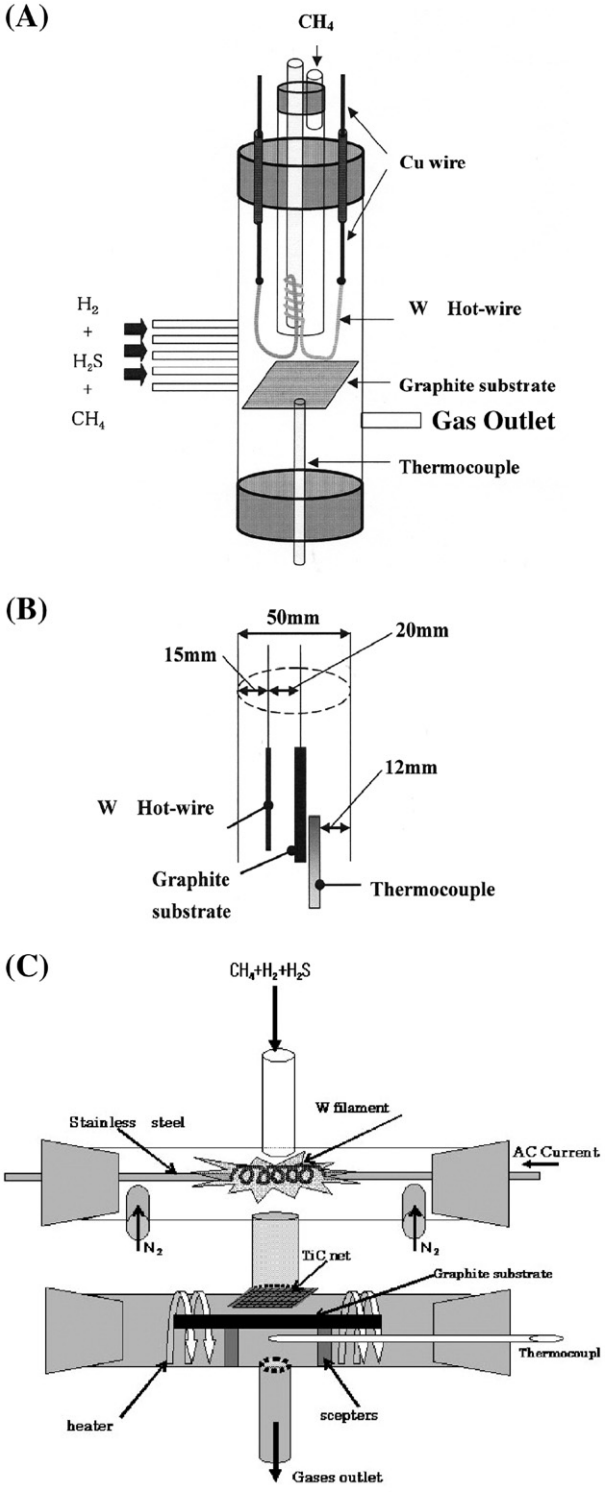


Fig. 1. Hot-wire CVD reaction apparatus for preparing CMCs.

source gas inlet and gas outlet, was heated by nichrome elements from the outside. Ni was sprayed on the graphite plate as the catalyst. The source gases were pre-decomposed by the hot wire then flowed to the lower reaction tube before filtrated through a Ti net. When the upper reaction tube reached 1500 °C and lower reaction tube reached 700–730 °C, the source gases were introduced into the system.

## 3. Results and discussion

Because the decomposed temperature of $CH_4$ is 1200 °C, which is much higher than $C_2H_2$, and at this temperature, the anisotropy [12] of the catalyst (i.e. different catalyst crystal face has different activation for carbon deposition), which is the driving force of coiling formation, is difficult to generate. Thus, a hot-wire CVD process, or preheated process was developed and employed to prepare CMCs using methane carbon source. If no preheating was employed, that is, when only the lower CVD reactor was used, only carbon nanofibers were obtained because at this high temperature the Ni catalytic anisotropy did not generate [12].

When using Reactor A, the total gas flow rates were set as: $N_2$ 800, $H_2$ 800–1280, $H_2S/H_2$ 100–200, $CH_4$ 300–600 sccm; reaction time is 30 min. Many experiments were carried out by changing the temperature and the gas flow rates, however, $CH_4$ was very difficult to be decomposed, and only a small amount of the deposit was obtained.

The Reactor B was also tried; the other reaction conditions were kept the same. Many experiments were also carried out by changing the temperature and the gas flow rates. There were more deposits obtained than that reactor A. A little amount of CMCs was obtained sometimes, co-depositing with carbon nanofibers as shown in Fig. 2, the SEM enlarged view shows that the coil wire morphology is quite interesting: these CMCs are double-helix, but coil wires seem to be composed of multiple sub-fibers, which are different from those CMCs prepared using $C_2H_2$.

Using Reactor C, the reaction time was 30–90 min; the flow rate of $N_2$, $H_2$, $H_2S$, and $CH_4$ was 150–200, 110, 30, 150 sccm, respectively. CMCs were synthesized in hundreds of milligram order in one batch, indicating that the preheated process in hot-wire CVD is an effective CVD process for producing CMCs using methane. When using acetylene as the carbon source, the optimum reaction temperature for producing CMCs is 750–780 °C. Catalytic anisotropy, which is the driving force of the coiling of the carbon fibers and is decided by the Ni–C–S–O quaternary compound layers on the surface of the respective crystal faces of the Ni catalyst is considered to be the largest in this temperature range. Accordingly, it may be reasonably

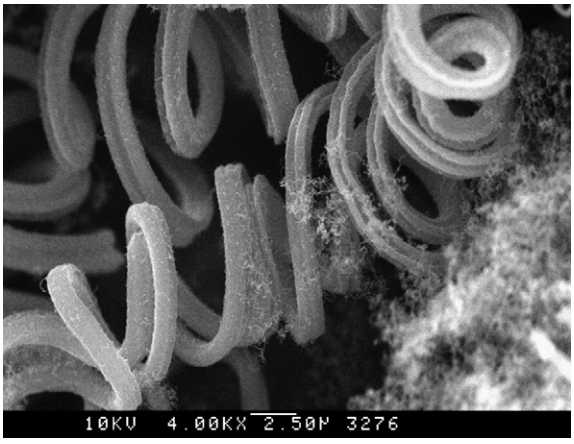


Fig. 2. Deposits obtained using Reactor B.