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Growth Kinetics of Carbon Microcoils
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Introduction
Bidirectionally grown double helical carbon nanofibers or carbon microcoils (CMCs) exhibit an intriguing morphology. CMCs are formed by unique catalytic mechanism during growth. Rotation of the catalyst was proposed by Chen et al. (Diamond Relat. Mater. 2003;12(10):1836-40). In this study, rotation speed of growth-tip and coil growth speed were estimated using growth model fitting.

Synthesis of CMCs
CMCs were synthesized using a chemical vapor deposition method. C-H2, Ar, H2 and thiophene (C2H2S) gases were heated with Ni catalytic powder on graphite substrate. A small amount of sulfur plays an important role to form bidirectionally grown double helical shape.

Characterization
As-grown carbon material has three layers (Fig.3a)
- Top layer ➔ CMCs
- Middle layer ➔ Carbon nanotubes and nanofibers
- Bottom layer ➔ Dense and shiny carbon materials including nickel

CMCs obtained at 740 °C
- Average coil diameter (d0) ➔ 2.86 μm
- Average fiber size (w × h) ➔ 0.59 × 0.94 μm²
- Volumetric density (ρ) ➔ 1.7 g/cm³
- The number of CMCs (N0) ➔ 3.31×10^5 cm²

Fig. 2. Optical microscope image of CMCs embedded in epoxy. To measure the number of CMCs (N0), as-grown carbon material was embedded in epoxy, and then the cross section was polished.

Growth Kinetics of CMCs

Growth Modeling

Three assumptions for CMC growth kinetic modeling
i. Catalyst poisoning is subjected to exponential decay.
ii. Every catalyst has same size and carbon deposition rate.
iii. The initial number of active catalyst is the same as the number of CMCs (N0).

From the assumptions, growth kinetic equation for CMC can be written as:

\[ W = W_{\infty} \left\{ 1 - \exp(-k_1(t - t_0)) \right\} \tag{1} \]

where \( W \) (mg/cm²) is the weight of CMCs, \( W_{\infty} \) (mg/cm²) is the weight of CMCs at \( t=\infty \), and \( k_1 \) (min⁻¹) is catalyst poisoning constant and \( t_0 \) (min) is timing at the start of growth of CMCs.

A constant of CMC growth rate per catalyst \( k_2 \) (mg/min) can be expressed as:

\[ k_2 = \frac{k_1 W_{\infty}}{N_0} \tag{2} \]

Factors for rotation of growth tip
- Growth of two curved nanofibers from one catalyst
- Fixation of bottom of coil by middle or bottom layer

Carbon deposition rate of each fiber (Fig. 6a)
- Half of carbon deposition (\( k_2/2 \)) from one catalyst was used to form one side of carbon fiber.

Rotation and growth speed at 740 °C (Fig. 6b)
Based on the CMC size, density (ρ) and carbon deposition rate per catalyst (\( k_2 \)), growth speeds were calculated.

- Rotation speed of catalyst ➔ 41.5 rpm
- Growth speed of coil length ➔ 78.1 μm/min

Conclusion
The growth mode of CMCs was bidirectional double helical growth. Exponential decay model was well fitted to weight gain of CMCs. Catalyst or growth tip was rotated by the formation of two curved carbon filaments and the fixation of the bottom part of the coil in carbon deposition. The rotation speed was calculated using parameters obtained from the experiments and curve fitting.