

Bamboo-Like Carbon fibers growth mechanism

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Abstract

Bamboo-like growth behavior of carbon fibers is explained. There is a requirement to have this type of growth: to operate above the Tammann temperature of the catalyst. The metal nanoparticle can change shape during reaction (sintering-like behavior) so that CNT growth adjusting geometry. At nanoscale, Fick's laws still apply. Nanoparticles with a diameter below 20 nm show a reduction of melting point (mp) and Tammann temperature (T_{Ta}).

1. Introduction

The mechanism of bamboo-like carbon nanotubes growth requires clarification. Detailed kinetic studies are an efficient key to understand a mechanism. This has been evidenced in catalytic graphene growth [1-3]. The main scope of the present proposal is to evidence the need to operate above the Tammann temperature to enable bamboo-like growth. A comprehensive review of CNTs bamboo-like growth has been published recently, covering design, synthesis and production methods [4]. The need to enable solid-state shape changes also led to the conclusion that in *carbon gasification* operating above Tammann temperature (T_{Ta}) is required to have efficient carbon/catalyst contact and so, good

catalytic activity: catalyst nanoparticles showing "carbon worm" behavior [5].

2. Growth of carbon nanotubes above catalyst's Tammann temperature.

The different role of the different crystal faces in catalytic carbon growth has been known for decades. Nickel has an fcc crystal structure. It is known that (111) faces facilitate nucleation and growth. Of the 3 alternative carbon growth routes (*catalytic*, *hybrid* and *pyrolytic* [1-3]) bamboo-like growth is usually a *hybrid* growth route mechanism, operating above the Tammann temperature of the catalyst particle being used. Values of the T_{Ta} for 10 metals are included in Table 1. Bamboo-like growth is an example of nanoparticle's shape changes by solid-solid interaction above T_{Ta} .

Crystal shape and crystal orientation of the faces of catalyst nanoparticle is crucial to get a desired shape and a fast rate of the growing graphene structure.

Shape changes due to contact interaction are facilitated above the Tammann temperature (Fig.1). Bamboo-like growth is a good example of the importance of T_{Ta} in shape adjustment of a nanoparticle by solid-solid interaction.

METAL	Melting ($^{\circ}\text{C}$)	T_{Ta} ($^{\circ}\text{C}$)
Fe	1538	632
(Fe ₃ C)	1223	475
Co	1495	611
Ni	1455	590
Cu	1083	405
Ru	2334	1030
Rh	1964	845
Pd	1555	641
Ag	962	346
Pt	1768	747
Au	1064	396

Table 1. Melting points and Tammann temperatures of metals frequently used.

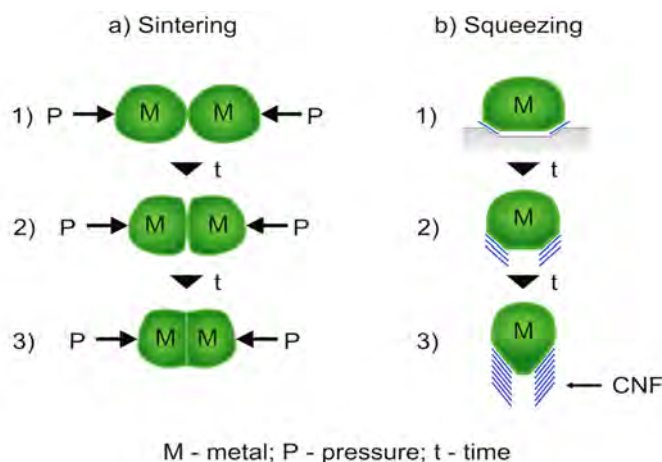


Figure 1. Shape changes of nanoparticles above the Tammann temperature under surface pressure.

3. Alternative types of growth and bamboo-like growth variant.

There are alternative types of multiple wall carbon nanotubes (check Table 2):

a) Tube growth by successive graphene layer nucleation and growth *below* the previous one, via the catalytic route or the **hybrid route**; b) Successive

pyrolytic formed layers grow via the **pyrolytic route** - over tubes previously formed (Fig. 2).

In the catalytic route or hybrid route a new graphene layer nucleates below the previous one, expands and bends by growth in the periphery, near the active catalyst surface border. This requires the formation of 6 pentagons at the periphery of the new expanding graphene layer.

KINETIC ROUTES	T range (°C)	C GROWTH TYPE	ACTIVE CATALYSTS
I Catalytic	300-550	Surface catalysis	Fe, Co, Ni
II Hybrid	550-(700)	C black atoms dissolve/grow	Pt, Ru, Mo, Ni, Cu...
III Pyrolytic	600-(1200)	C black forms layers	No catalysis, shape adjusts

Table 2. Alternative graphene formation routes.

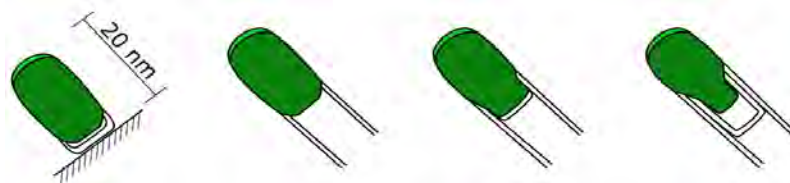


Figura 2. Bamboo-like CNT growth. After a 1st graphene nucleus and 90° bending (6 pentagons) a second nucleation is formed 15 minutes later.

In Table 3 we list 21 bamboo-like growth studies, including the work of Lee et al. in 2000 (C₂H₂, Fe, 750-950 °C) In our view, these authors proposed a correct approach to the mechanism. The studies of Saito in 1995 [18] and Li et al. in 1999 [19] gave interesting information about growth modes and clues to understand the carbon growth mechanism. Two carbon growth alternatives - octopus carbon (formed

at 500 °C) vs. bamboo-like (formed at 650 °C) - with the same gas (CH₄/N₂) and the same catalyst (Ni-Cu) evidenced kinetics and geometry roles. Octopus carbon requires easy and selective carbon nucleation on the 8 (111) facets [5]. A scheme of bamboo-like growth initiation is shown in Fig. 4, adapted from He et al. [21].

CATALYST	GAS	T °C	1st author	Year	Ref-
Ni-Cu/Al	CH ₄ /N ₂	500-730	Li YD	1999	[18]
Fe/SiO ₂	C ₂ H ₂	750-950	Lee CJ	2000	[6]
Fe/SiO ₂	CH ₄ /NH ₃	650-950	Cui H	2000	[20]
Ni-Cu/Al ₂ O ₃	CH ₄ /H ₂	720-830	Chen J	2001	[21]
Ni	C ₂ H ₂ /N ₂ /H ₂	750-950	Jung M	2001	[33]
Ni	Phthalocyanine	600-850	Katayama T	2002	[22]
Co/Al ₂ O ₃ -Ti	C ₂ H ₂ /NH ₃	750-950	Jang JY	2002	[23]
Fe, Co, Ni	CH ₄ /H ₂	850-1100	Bartsch K	2005	[35]
Fe	C ₂ H ₂ /NH ₃ /H ₂	700	Ting JM	2007	[24]
Ni	C ₂ H ₂	650	Lin MT	2007	[25]
Ni/Al	CH ₄ /N ₂	500-600	He C	2007	[19]
Cu	CH ₄ /H ₂ /H ₂ S	500-900	Katar SL	2008	[26]
Cu/Al ₂ O ₃	C ₂ H ₅ OH	700-850	Xue B	2009	[34]
Ni (AC) ₂	C ₄ H ₄ S/H ₂ -S	Detonation	Wang C	2010	[37]
Ni, Ni-Cu	CH ₄ /N ₂	550-830	Gonzalez I	2011	[8]
Cu/Al ₂ O ₃	C ₂ H ₄ /He	700-900	Lin JH	2012	[27]
Fe, Co, Ni, Al ₂ O ₃	C ₂ H ₂	720	Kekzenovity	2013	[28]
Cu/SiO ₂	C ₂ H ₄ /He	500-900	Lin YC	2013	[29]
Cu/Al ₂ O ₃	C ₂ H ₂ /N ₂	550-800	Krishna VM	2014	[30]
La/NiO ₃	Glicerol/Ethanol	700-900	Velasquez	2014	[36]
Fe-Mo/Al ₂ O ₃	C ₃ H ₄ N ₂	800-900	Wang Q	2017	[31]
Fe/Al ₂ O ₃	Polyamide	750	Arnaiz N	2018	[32]

Table 3. A selection of bamboo-like CNTs growth studies. Operating temperatures are always above the Tammann temperature of the metal (see Table 2) facilitating shape adjustment of the particle and 90° turning in graphene growth.

CNF growth includes a graphene layer that covers the tip and an extension: a conical catalyst shape graphene layer. The adjustment is possible due to sintering-like reshaping of the metal nanoparticle, but growth of the more regular CNT structure is not possible. In this case the structure must include pentagons and heptagons to adjust the growing graphene layer to the conical shape.

Table 3 evidences that successful experiments to produce bamboo-like nanotubes are run above catalyst's T_{Ta} . So, catalyst particles can change shape progressively under pressure, like in sintering. At nanoscale the change of *shape* is much easier. Li et al. used Ni with about 18% Cu [18], which lowers mp and T_{Ta} of Ni-Cu alloy compared to pure Ni.

Conclusions

1. Bamboo-like growth behavior of carbon fibers occurs most likely by a sintering-like shape change mechanism of the catalyst particles, enabling a new graphene layer to bend and grow further (inside). This is possible above the Tammann temperature of the metal particle under *catalytic* or *hybrid* carbon growth routes but not under *pyrolytic* growth. Shape changes are not due to liquefaction but to movements of the metal atoms of the external layer of the catalyst nanoparticle - under surface contact pressure.

2. This sintering-like behavior should not be described as melting or liquid-like behavior. Catalysis by solids is based on a surface structure: liquids do not have a stable surface structure.

3. Kinetics is a key to understand the behavior observed, particularly the concept of rate determining-step. Isothermal kinetic studies are required. Scanning temperature studies give useful *initial* information. However, reaction orders and activation energy evaluation in new systems require *isothermal* experiments.

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