

# Synthesis of Beaded and Entwined Carbon Nanofibers in Ni : Al Alloy Catalyst

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This paper reports two new types of carbon nanofibers synthesis by thermal decomposition of *n*-hexane in presence of Ni–Al alloy in hydrogen atmosphere at 1100 °C. One type is "beaded fibers" in which spherical carbon beads (~1  $\mu$ m) are regularly grown from outer surface of fibers (~0.3  $\mu$ m). The other new microstructure is "entwined fibers" in which multiple nanofibers of diameter ~100 nm grow self-entwined like a braid of hair. Both bead-fiber bonding (in beaded fibers) and fiber–fiber interaction (in entwined fibers) are strong to be detached/unfolded by 30-min ultrasonication.

Keywords: Carbon Fibers, Chemical Vapor Deposition, Electron Microscopy.

## 1. INTRODUCTION

In the recent past many novel carbon nano-materials came to existence, viz. fullerene,<sup>1</sup> nanotube,<sup>2</sup> etc. Although there are a number of techniques that have been used to synthesize these materials, arc-discharge,<sup>2</sup> chemical vapor deposition (CVD),<sup>3</sup> and laser vaporization<sup>4</sup> are common. Carbon onion,<sup>5</sup> nanocapsules,<sup>6</sup> nanocones,<sup>7</sup> nanohorns,<sup>8</sup> nanospring,<sup>9</sup> and nano-octopus type fibers<sup>10</sup> are some different kinds of carbon structure emerged lately while synthesizing and studying fullerene or nanotube. The formation of these unusual carbon nano-structures are mainly due to the wide variation of parameters used in the synthesis process. Out of many parameters involved in CVD synthesis of carbon nano materials, catalyst, temperature, precursor, carrier gas, and its flow rate are crucial. Usually, transition metals or their alloy of different compositions are widely used as a catalyst for the synthesis of carbon nanotubes (CNTs) and nanofibers. Although nanotubes have been used for many applications, vapor grown carbon fibers are found to be applicable in the lithium rechargeable cell,<sup>11</sup> hydrogen storage,<sup>12</sup> electron field emission,<sup>13</sup> and also in composite materials.<sup>14</sup>

Unlike mono-metallic catalyst that produces regular carbon nanostructures i.e., MWNTs, SWNTs, and carbon fibers, alloy catalyst produces more novel carbon structures. Binary or multinary alloy with every component having catalytic role has been employed extensively for

synthesizing carbon nano structures.<sup>15-19</sup> However, little has been carried out using alloy catalyst where one component has almost no catalytic role. We have reported the growth of octopus-like branched fibers from Ni-Cu alloy catalyst.<sup>10</sup> Recently Kevin et al. has also reported branched carbon nano structure using same Ni-Cu alloy catalyst.<sup>20</sup> Despite the fact that copper independently does not show a good catalytic effect for the growth of nanotube or nanofiber, in its alloy with nickel, it incites a branched structure.<sup>10, 20</sup> On the same line, in the present study Ni-Al alloy was chosen to investigate its effect in the growth of carbon nanostructures. In the alloy of Ni-Al, aluminum alone does not act as a catalyst but affects the catalytic role of Ni leading to the formation of diversified nanostructures. As for carbon precursor, there are many hydrocarbon solvents and gases that have been used for the synthesis of carbon nanomaterials. Ajayan et al. have shown a high growth rate in the formation of long single walled nanotube strands using *n*-hexane as a precursor and ferrocene as a catalyst.<sup>21</sup> Due to lower boiling point and higher vapor pressure of *n*-hexane, it was found relatively better precursor than other solvents. Hence *n*-hexane was chosen as a carbon source with the novel use of Ni-Al alloy catalyst in the present study.

### 2. EXPERIMENTAL DETAILS

The synthesis was performed in a quartz tube inserted in a horizontal tubular electric furnace using catalyst coated silicon wafer (100) as a substrate. Catalyst (Ni–Al alloy

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powder) was first dispersed in acetone and then sprayed over silicon wafers to get a thin coating on it. As-prepared substrate was then transferred to the quartz tube. Prior to deposition, furnace was slowly heated to 900–1100 °C under a hydrogen flow of 0.2 ml/min. Holding it at a desired high temperature for 15 min under hydrogen flow, argon was passed through n-hexane solvent at the same flow rate of 0.2 ml/min for the next 15 min. After this total of 30 min reaction time, argon flow was stopped and furnace was allowed to cool under the continued hydrogenflow. After cooling down to room temperature, hydrogen flow was stopped and carbon deposited substrate was taken out for the characterizations.

Ni : Al alloy catalyst (50 : 50) used in this study was bought from SISCO Research Laboratories Pvt. Ltd., Bombay, India. X-ray diffraction (XRD) study of same powder was carried out with a Philips X'pert diffractometer (Cu-K<sub> $\alpha$ </sub> target used for X-rays) to ascertain the different phases of alloy. A Topcon ABT-150F scanning electron microscope was used at 10 kV accelerating voltage for surface morphology of carbon samples synthesized in the present study. Transmission electron microscopic analysis was carried out with a PHILIPS CM200 TEM at an accelerating voltage of 200 kV. TEM samples were prepared by ultrasonic dispersion of powder carbon samples in isopropanol solvent and then transferring a drop of solution onto carbon coated micro grids.

### 3. RESULTS AND DISCUSSION

Figure 1 shows the XRD spectra of Ni–Al alloy used as a catalyst for the production of carbon nanomaterials in the present study. It is found that  $Ni_2Al_3$  phase (JCPDS, PDF 14-0648) is more prominent than Ni–Al phase (JCPDS, PDF 44-1188). The corresponding crystal planes of  $Ni_2Al_3$  and NiAl are assigned in the figure.

Figure 2(a, b) shows the carbon nanostructures formed at a deposition temperature of 900 °C. A poor growth of fibers is observed with plenty of amorphous like carbon. Fibers obtained in this case are of diameter around 100 nm. In contrast, at 1100 °C there is a clear dominance



Fig. 1. X-ray diffraction profiles of Ni: Al alloy powder used as a catalyst for the synthesis of carbon nanostructured materials.

of fiber formation (Fig. 2(c-f)). This is due to the melting point of Ni<sub>2</sub>Al<sub>3</sub> (1133 °C),<sup>22</sup> that is close to the pyrolysis temperature (1100 °C). This distinctly indicates the vapor-liquid-solid mechanism involved in the formation of these fibers.<sup>23</sup> As the decomposition of hydrocarbon vapor on metal particles is an exothermic process, the present growth seems to be taking place at the melting temperature of Ni<sub>2</sub>Al<sub>3</sub> alloy phase. Therefore there is a high yield of fiber formation with no other carbonaceous structure observed under microscope when growth was carried out at 1100 °C. On the other hand, low-temperature growth mechanism must be associated with solid metal particles. However, effect of precursor i.e., n-hexane cannot be ignored too. It supports previous report of formation of nanotube at higher temperature (1150 °C)<sup>21</sup> indicating higher decomposition temperature of *n*-hexane than commonly used other hydrocarbon solvents.

Two new types of fibers formed at 1100 °C are depicted in Figure 2(c-f). One type may be called "beaded fibers" (Fig. 2(c, d)) in which spherical carbon beads (~1  $\mu$ m diameter) are regularly grown from fairly uniform (~0.3  $\mu$ m diameter) fibers. The other type of new microstructure obtained here may be called "entwined fibers" (Fig. 2(e, f)) in which ~100 nm thick fibers are self-entwined presenting a challenging puzzle to be resolved. The growth mechanism must be complicated and yet unknown. From the microscopic observation, the volume ratio of beaded and entwined fibers was estimated to be 1:1.

Figure 3 shows typical TEM images of beaded carbon fibers. Spherical beads are grown to fibers on either side, as also seen in their SEM images (Fig. 2(c, d)). In Figure 3(a), there are two fibers closely attached each other and spherical beads are also seen to be grown from each fiber. Similarly in Figure 3(b), two straight carbon fibers are bonded and spherical beads have grown on the surface of fibers. Inset of Figure 3(a) shows a selected area diffraction (SAD) pattern of the beaded fiber. Although the crystal fringe obtained here is not sharp enough as that of pure graphite, it is not entirely amorphous either. It was confirmed by taking extensive TEM images with corresponding SAD patterns that there was no metal content inside the carbon beads or fibers. Figure 3(c) shows a magnified image of junction from where growth of beads taking place from a single fiber.

Figure 4 shows typical TEM images of entwined fibers. Multiple nanofibers ( $\sim$ 100 nm diameter each) are selfentwined in a regular manner (Fig. 4(a, b)). Careful observation at high magnifications revealed presence of some branched segments as well (Fig. 4(c)), amid the entwined ones. However, mostly they are entwined like braided hair. Like that of a beaded fiber, the SAD patter of this entwined fiber as well reflects its poor graphitization.

To get an idea about how strong this bead-fiber bonding is (in beaded fibers) or how strong the fiber–fiber interaction is (in entwined fibers), those were ultrasonicated



Fig. 2. SEM micrographs of carbon fibers: (a, b) Submicron order coiled fibers formed along with plenty of amorphous like carbon at 900 °C; (c, d) Beaded carbon fibers formed at 1100 °C; (e, f) Entwined fibers formed at 1100 °C.

(ultrasonication bath power 120 W and frequency 34 KHz) for 30 min in iso-propanol and then reexamined under transmission electron microscope. There was no considerable change in the nature and quality of the fibers observed. Not a single isolated bead was found under microscope, which suggests a strong bonding between the beads and fibers. Only a few strings of beads were seen (Fig. 5(a)) which were most probably detached from their fiber base because of their long length and heavy weight, but single-beads grown on the fiber remained intact. Similarly, individual fibers of the entwined one did not unfold/disperse (Fig. 5(b)), which is more a reason to believe them to be an organized novel structure.

Jacobsen and Monthioux reported "beaded cones" microstructures where a cone like sharp needle was protruded from a spherical carbon bead in the by-products of vapor grown carbon fiber experiments at 1100 °C from methane and hydrogen.<sup>24</sup> Further, Ci et al. have reported spindle like thickening inside carbon filaments when benzene was pyrolysed in presence of ferrocene in a temperature range of 1100-1200 °C.25 Ting et al. also reported similar kind of beaded carbon tubes using iron catalyst and methane precursor in hydrogen atmosphere.<sup>26</sup> In all those cases carbon beads were grown inside the fibers or fibers were thickened at some intervals. In no cases, growth of beads has been reported to occur on the fiber surface. Nevertheless, previously we had reported formation of isolated beads from camphor (in an entirely different experimental

condition).<sup>27</sup> In that case no fibers were formed except but spherical beads, whose central black core was analyzed to be amorphous, whereas the surrounding gray shell was found to be turbostratic graphite layer. In the present case, although no isolated beads are observed, they are found to grow on the surface of carbon fibers. The growth of these beaded fibers is believed to be effect of novel alloy catalyst. It is interesting to note that the spherical carbon beads are preferentially grown on the submicron fibers. This may be attributed to the defect sites on the surface of sub-micron fibers. It is well known that accumulation of particles is favored on the surface sites having higher free energy and therefore growth and nucleation of carbon beads occurs from those sites.

Tip- and base-growth mechanisms are widely explained in the formation of carbon fibers.<sup>28-30</sup> In the tip growth mode, a catalyst particle is found at the tip of the fibers. Generally, this growth mechanism is reflected when organometallic catalyst (viz. ferrocene, cobaltocene, nickelocene, etc.) are used in powder form (whose vapor provides floating catalyst particles) or if interaction between substrate and the catalyst particle is poor (i.e., contact angle of catalyst material to the substrate surface is less than 90°).<sup>30</sup> In the base growth mechanism, catalyst particles remain intact on the base due to strong catalystsupport interaction. In present study, since no catalyst particles were observed on the fiber tips (Fig. 5(b)), base growth mechanism applies to these novel fibers. When it



comes to explain the absence of metal particles in the present observation, it is worth considering that the catalyst here is in the form of a thin film on the Si substrate, which reduces the probability of catalyst particles in manifolds.

It is pertinent to compare the present study (exploiting Ni–Al alloy) with our previous report in which octopuslike carbon fibers were grown by almost similar method (using Ni-electroplated Cu substrate forming Ni–Cu alloy).<sup>10</sup> From the catalyst point of view, one aspect is common: In both the cases, one component of the alloy used is non-catalytic (Cu and Al), whereas the second component (Ni) is a well recognized catalyst for the formation of carbon nanostructures. However, the resulting products are quite different. Use of copper with nickel leads to octopus-like branched structures, whereas aluminum with nickel results in present beaded and entwined fibers. Apparently aluminum chemistry seems to be responsible

**Fig. 5.** TEM images of the products after 30-min sonication: (a) Heavy strings of beads detached from the beaded fiber but not the single beads; (b) Entwined fibers still maintained their organization.

for the entwining, however, involvement of other factors (precursor, Si substrate and high temperature, etc.) cannot be ruled out. There is no report on the formation of these novel structures and it is early to predict any growth mechanism.

## 4. CONCLUSIONS

In summary, present study reveals that a bi-metallic alloy with one metal having non-catalytic effect could be used for growing new types of carbon nanostructures. Ni–Al alloy catalyst chosen in this work for the synthesis of carbon nanomaterials leads to the formation of two new types of fibers. Higher temperature (1100  $^{\circ}$ C) is found to be

favorable for the growth of beaded and entwined fibers. The growth of spherical beads on the sub-micron fibers are attributed to the presence of defect sites on it. Nonisolation of beads from the fiber base or individual fibers of the entwined one even after 30-min-long ultrasonic agitation suggests a strong bead-fiber bonding as well as fiberfiber interaction.

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