

## Controlled Flame Synthesis of Carbon-Microstructures

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**ABSTRACT:** In this study the effects of fuel equivalence ratio, residence time and type of metal catalyst on the controlled flame synthesis of carbon microstructures are studied. A premixed propane/oxygen flame stabilized on a water-cooled flat flame burner was selected for the study. Three catalysts, Ni (99.8% pure) with dia 1.0mm, Stainless steel (Unibraze ER316) with dia 0.68mm and Monel (Unibraze 60 ERrNiCu-7) with dia 2.5mm were used for the nucleation and growth of the carbon microstructures. Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) were utilized for the characterization of the sampled structures. The results revealed the following: (a) highly ordered microstructures in terms of helicity, spirality and vertical alignment were achieved, with optimum fuel equivalence ratio 1.9 using Nickel, Stainless Steel and Monel wires; (b) for the same conditions the vertically aligned microstructures consist of compact bundles of individual hollow tubes and (c) a yield of 2mg/min with Monel wire of 2.5mm diameter was possible.

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### I. INTRODUCTION

Ever since their discovery of Carbon nanotubes, synthesis of carbon-microstructures have attracted significant attention due to their striking properties. Large quantities of these carbon microstructures are needed in order to make their applications viable and cost effective.

Current synthesis methods such as arc - discharge, chemical vapor deposition and laser ablation possess the disadvantages of short tube lengths, inherent defects and high costs. On the other hand, flame synthesis yields structures with low density, high specific surface area and it is more cost effective.

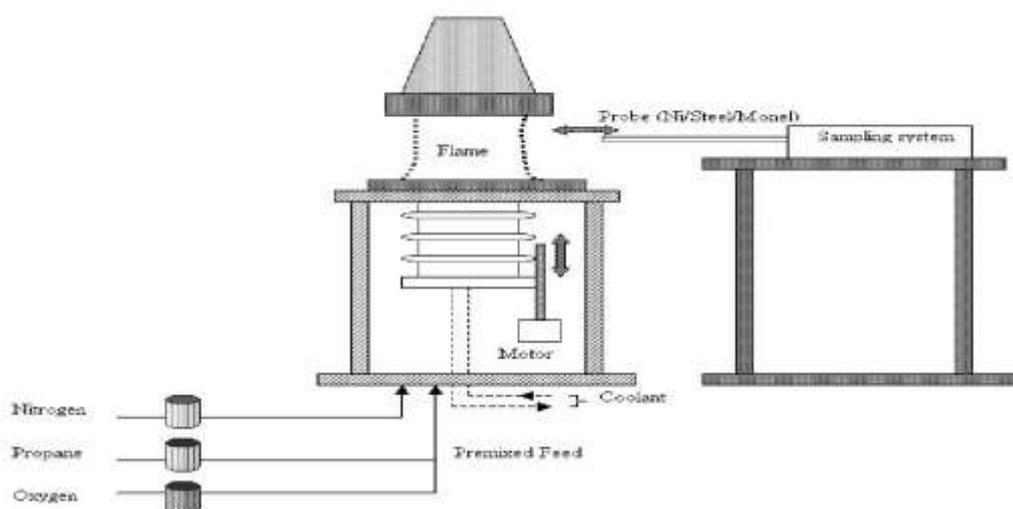
The earliest observation of tube like carbon microstructures in flames was reported by Singer [2], and since the 1990's several studies there have been reported on the synthesis of such structures in flames [3-8]. In flame synthesis of carbon microstructures premixed flame are preferred instead of the diffusion flames. This is because in premixed flames: (a) The chemical composition of products and reactants can be better controlled, and b) The temperature profiles are one-dimensional [9].

Thus, a premixed propane /oxygen flame was selected for the synthesis of carbon microstructures in the present study. Metal wires consisting of (a) Ni (98%pure), (b) stainless steel unibraze ER316 (Fe/Ni/Cu), and(c) Monel unibraze 60 ERrNiCu-7 were used as catalysts. The Carbon microstructures were characterized for their morphology and structures using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The experimental set up used in this study is discussed in the next section.

### Experimental Set-Up

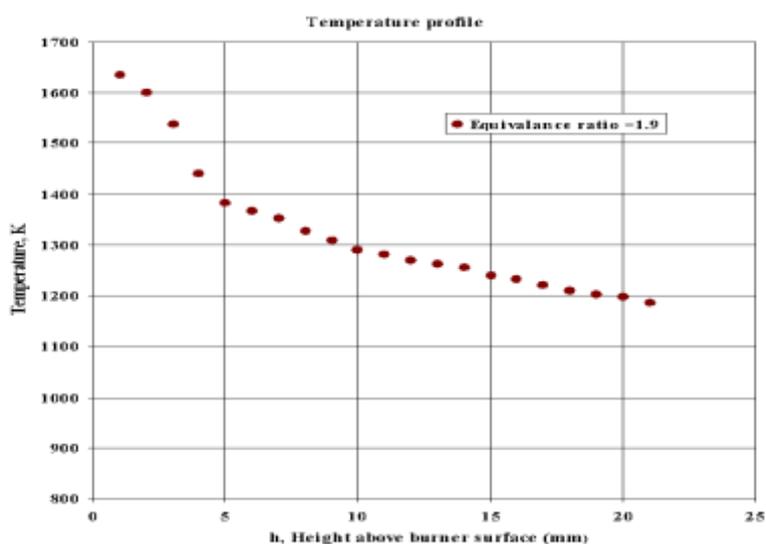
The experimental set up used is as shown in Fig 1. A flame was set up on a flat flame burner. A stainless steel chamber encases a sintered bronze plug (60 mm diameter) through which the premixed fuel and oxidizer flow. In order to prevent any flashback and to preserve its integrity, the plug is embedded with copper tubing through which cooling water circulates. In addition, the steel casing also houses an annular bronze plug where nitrogen is passed to prevent entrainment of outside air into the flame. The cold premixed gas velocity of 3cm/sec was chosen for this study. The experiment was performed for fuel equivalence ratio  $\phi$  ranging from 1.8 to 2.1.

The sampling system used in this study is a simple bar sliding mechanism on which the required catalyst wires or probes were mounted as shown in Fig. 1. The collected material on the wires was then transferred into a glass vial and taken for SEM and TEM analysis.



**Figure 1:** Schematic of Experimental set-up

The temperature measurements were performed with a platinum-10% rhodium thermocouple and were corrected for radiation losses. The temperature profile for equivalence ratio  $\phi = 1.9$  are shown in Fig 2 as a function of height above the burner.



**Figure 2.** Temperature Profile

## II. RESULTS AND DISCUSSIONS

The material deposited on Nickel grid (3.0mm diam), Stainless steel wire (0.68mm dia), pure Ni-99.8% (1.0mm dia) and Monel (Ni/Cu/Fe) (2.5mm dia) were imaged using SEM, to characterize the structure and morphology of the microstructures. The material deposited on the nickel grid was negligible. Thus, in order to increase the yield of carbon microstructures the amount of catalyst supplied and the sampling times had to be increased, so the choice was to use Nickel, Monel and Steel wires extensively in order to collect sufficient amount of material for further analysis.

### Effect of Catalyst Composition and Local Flame Conditions on the Morphology

In this investigation the effect of catalyst particles on the morphology of the microstructure with different residence and sampling times and with increasing  $\phi$  along the flame centreline was studied.

### Catalyst and Carbon Microstructure Morphology

As shown in Fig 3 Multi Walled Micro Tubes (MWMTs) are grown on Ni-grid when exposed to the flame for less than a minute. Nickel and Monel (Ni/Cu/Fe) wires produced helical, spiral and zigzag micro tubes as shown in Fig 4 and 5 respectively.

On the other hand, stainless steel wire enabled the growth of straight and aligned micro tubes as shown in Fig 6 .The white dots observed at the tip of the tubes in the SEM images are the catalyst particles. With Steel as catalyst material a layer of catalyst particles are seen at the tip of the compact bundle of the tubes as shown in Fig 6.

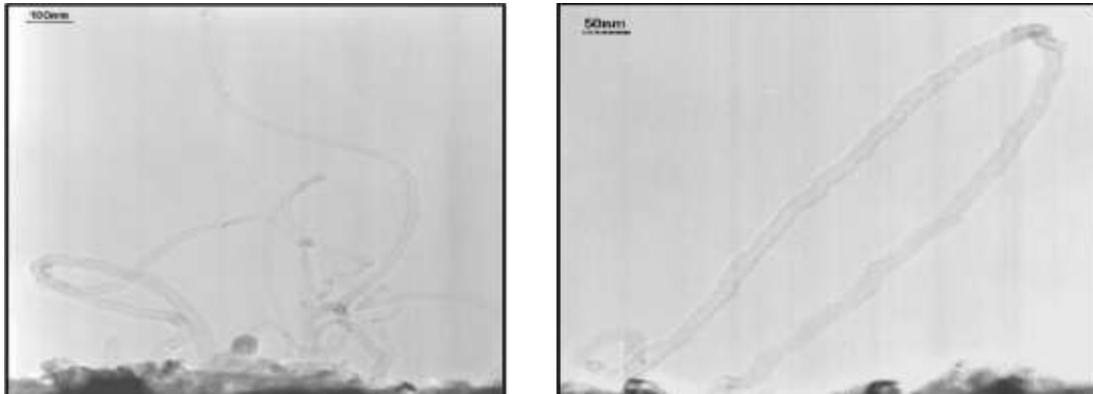


Figure 3: TEM images of MWMTs grown on Ni-grid at  $\phi = 1.9$ ,  $t = < 1$ min,  $h = 15$ mm.

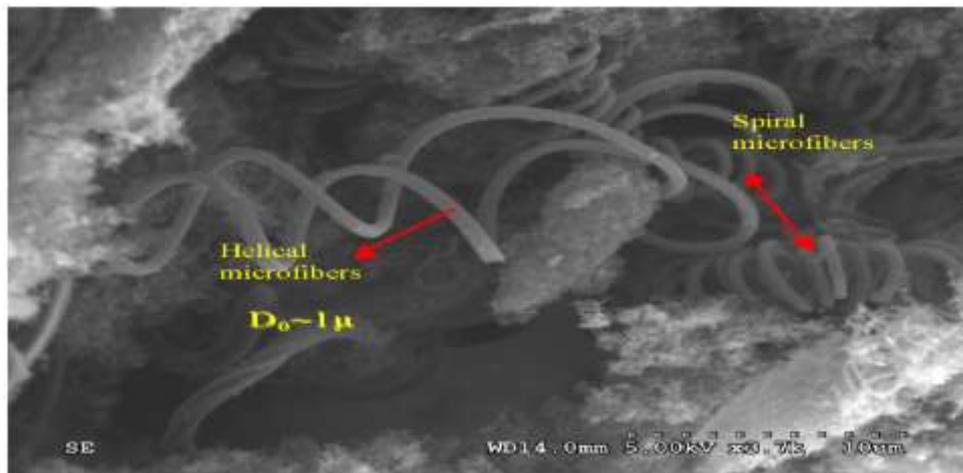


Figure 4: SEM images of Helical and spiral nanotubes with Ni-wire, with  $\phi = 1.9$ ,  $t = 10$ min,  $h = 15$ mm.

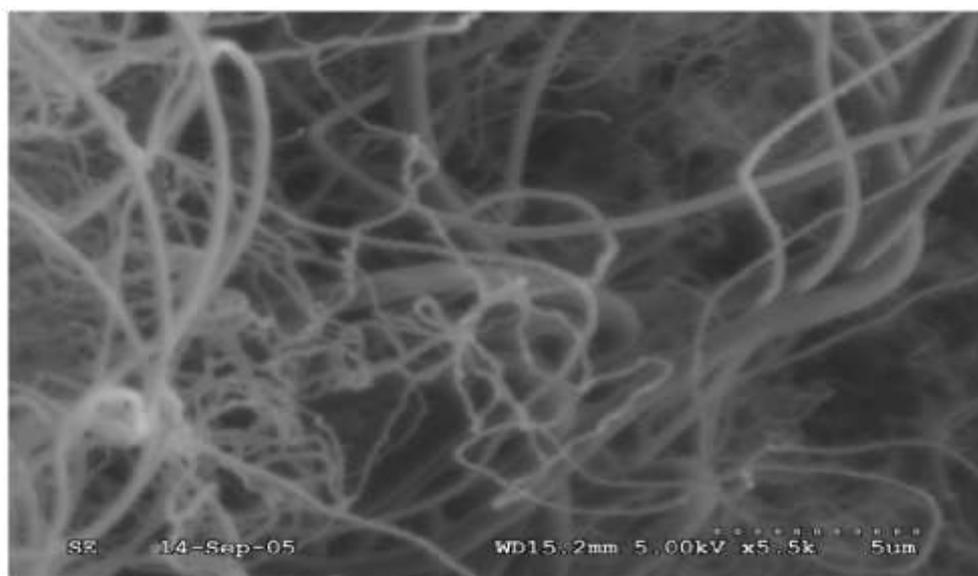
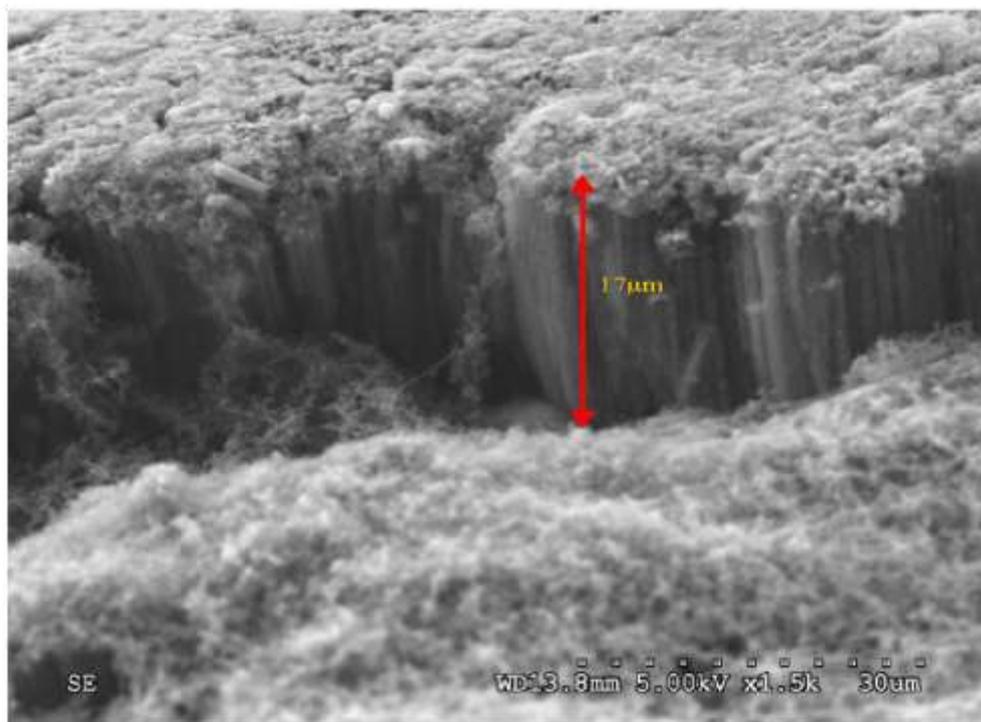


Figure 5: Spiral nanotubes with Monel-wire with  $\phi = 1.9$ ,  $t = 10$ min,  $h = 15$ mm

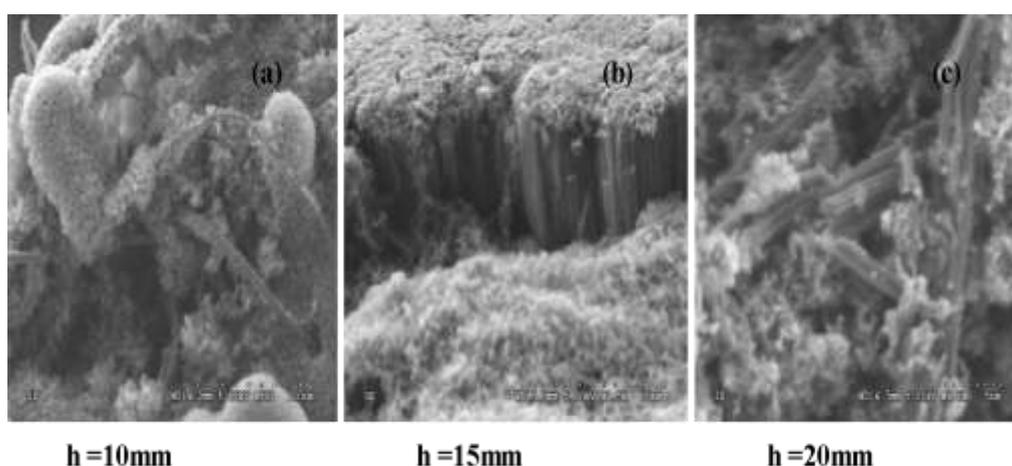


**Figure 6:** SEM image of aligned microfibers on Steel wire with  $\phi = 1.9$ ,  $t = 15$ min,  $h = 15$ mm

#### Variation of Microfibers Morphology with Residence Times

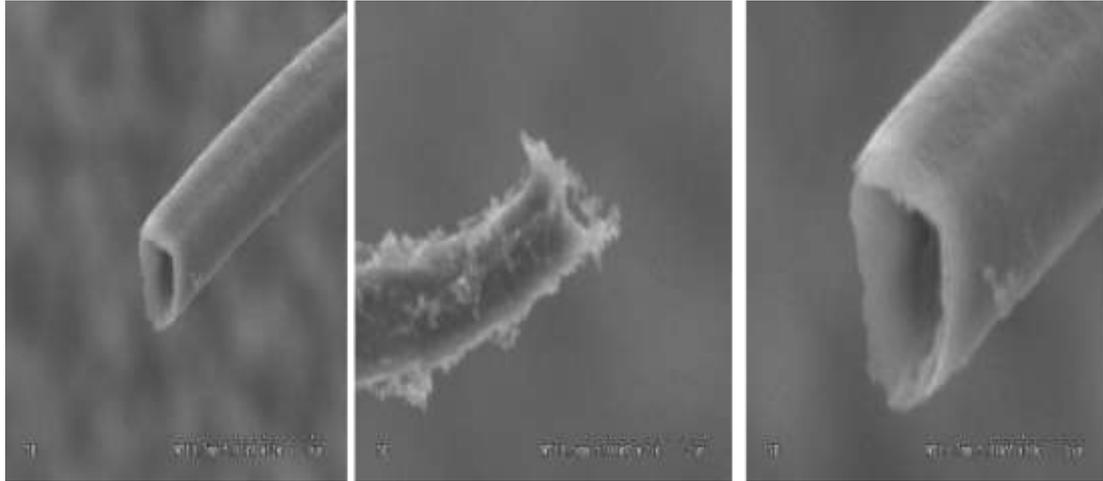
There were no filamental structures found on the Nickel, Monel and steel wires at a height of 5mm above the burner for  $\phi = 1.9$ . The temperature at this location was measured to be 1382°K, with an S-type thermocouple. With melting point temperatures of Steel and Ni wires being ~1420°K and 1726°K respectively, enough catalytic particles are generated but it is likely that insufficient population of precursors would not have facilitated the growth of the microstructures.

At 10mm height above the burner with Steel as a catalyst material, long and entangled microfibers, as shown in Fig 7 (a), were produced. At 15mm height above the burner aligned nanotubes of short lengths are seen as in Fig 7 (b), whereas at 20mm height above the burner bundles of straight nanotubes are present as shown in Fig 7(c). The temperatures at these locations were 1240 K (at 15mm) and 1197 K (20mm) respectively.



**Figure 7:** SEM images of microfibers with Steel- wire for  $\phi = 1.9$ ,  $t = 15$ min,  $h = 15$ mm.

While there was not noticeable change in the shape and size of the microfibers produced with Ni and Monel wires with increased residence times, these carbon microfibers were hollow in nature as shown in Fig 8.



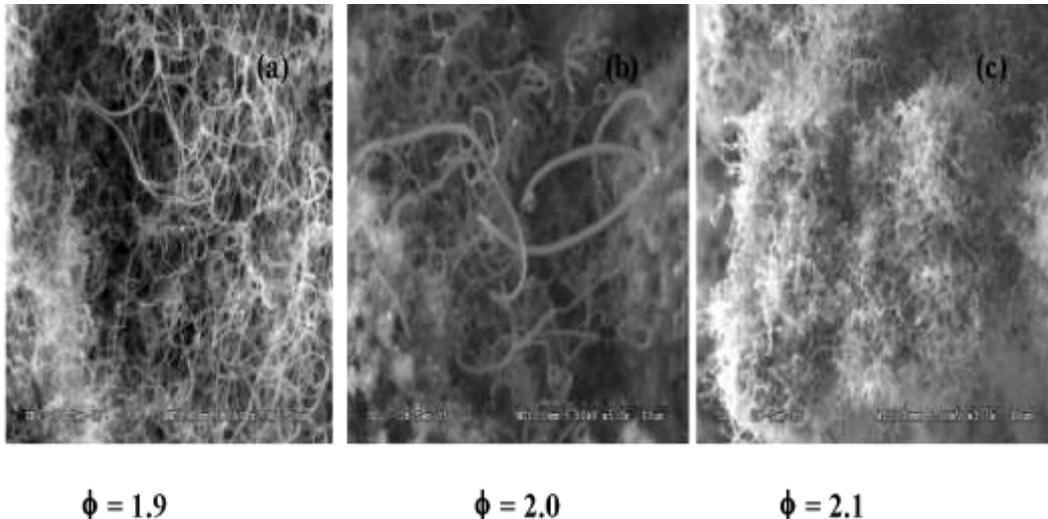
**Figure 8:** Hollow carbon microfibers

#### **Effect of Probe Exposure Time on the Microfiber Morphology**

When the probes were exposed for 5min in the flame at 15mm height above the burner for  $\phi = 1.9$ , very few nanofibers were found when compared to those produced for 10 min exposure. With increase in sampling times these fibers grew larger in diameters, and their degree of helicity and spirality increased. The growth rate of these structures was observed to be 168nm/min

#### **Effect of Fuel Equivalence Ratio on the CNT Morphology**

As may be seen from Fig. 9 for fuel equivalence ratios  $\phi$  larger than 1.9, the carbon nanofibers diameters, lengths and yield decreased. This trend can be attributed to the fact that with increasing  $\phi$  the presence of soot dominates the growth of carbon microstructures. Furthermore the temperature in the respective flame location decreases with increasing  $\phi$ . Thus the number of catalyst particles, which act as nucleation sites for growth of these microfibers is depleted.



$\phi = 1.9$

$\phi = 2.0$

$\phi = 2.1$

**Figure 9:** SEM images of Carbon Microfibers with increasing  $\phi$ .

### **III. DISCUSSION**

The formation of carbon into multiwalled micro tubes and microfibers in this experiment was found to depend upon the catalyst particle size, residence time, temperature and stoichiometry. These carbon microstructures followed the tip growth mechanism with a catalyst particle at the tip of the tubes. Growth of carbon microstructures formed can be explained via the carbon solvation, diffusion and precipitation mechanism [10].

Carbon solvation, diffusion and precipitation growth mechanism, shown in Table1 [10], occurs on suspended catalysts whose size exceeds 5nm. The carbon in this mechanism would originate from acetylene, which solvates into the particle and diffuses through the interstitial sites. When saturation occurs it precipitates out of the catalyst particle to grow MWMT and microfibers whose cross section and number of walls matches

with the crystallographic interstitial planes through which the carbon precipitated out to the catalyst particle [11]. This is a general case with nickel, which through observations was hypothesized that the growth of carbon micro tubes with demands of longer time, and thus nickel grows larger and more crystalline when compared with iron particles [12].

Base and Tip growth mechanisms as shown in Table1 [13, 9] occur on deposited catalyst particles via three steps. In the first step carbon solvates and diffuses through the catalyst particles. In the second step the growth of tubes depends upon the source of carbon available. In abundance of acetylene, a layer of amorphous carbon over the catalyst particle forms. Hence, carbon can solvate through the substrate only. In the third step when carbon precipitates out of the catalyst particle it would displace the layer of amorphous carbon away from the catalyst particle, thus leaving the particle at the base, whereas the amorphous layer forms a cap. In abundance of CO, continuous layers of amorphous carbon are etched from the surface hence carbon can solvate into the particle from the gaseous interface and precipitate on the opposite side of the particle, hence upholding the particle at the tip [12].

**Table 1: Growth Mechanisms**

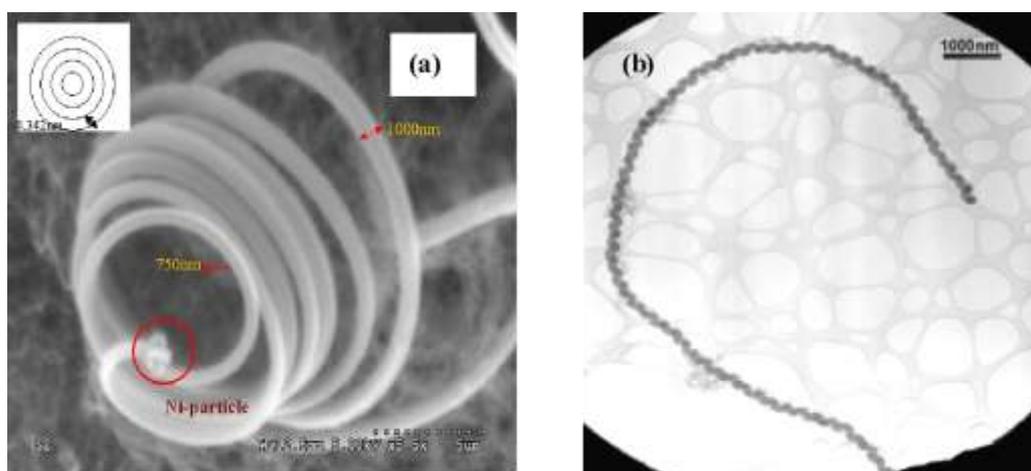
Carbon solvation diffusion & Precipitation [10]	Base growth Mechanism [11]	Tip growth Mechanism [9]
<ul style="list-style-type: none"> <li>&gt; Suspended particles</li> <li>&gt; Nanoparticle size &gt;5nm</li> <li>&gt; Interstitial diffusion</li> <li>&gt; Time scale~0.01ms</li> <li>&gt; MWNTs, CNFs.</li> </ul>	<ul style="list-style-type: none"> <li>&gt; Deposited Catalyst particles.</li> <li>&gt; C<sub>2</sub>H<sub>2</sub> layer formed</li> </ul>	<ul style="list-style-type: none"> <li>&gt; Deposited Catalyst particles.</li> <li>&gt; Amorphous carbon layers are etched from the surface.</li> </ul>

The size of catalyst particle increased with increase in sampling time. Depending upon the size of the catalyst particle the type of carbon structures formed differed as multiwalled nanotubes or nanofibers.

**Table 2: Sampling Time vs diameter of the Carbon Nanofibers**

Sampling Times	Diameter of Carbon Microfibers
5min	660nm
10min	1.5µm

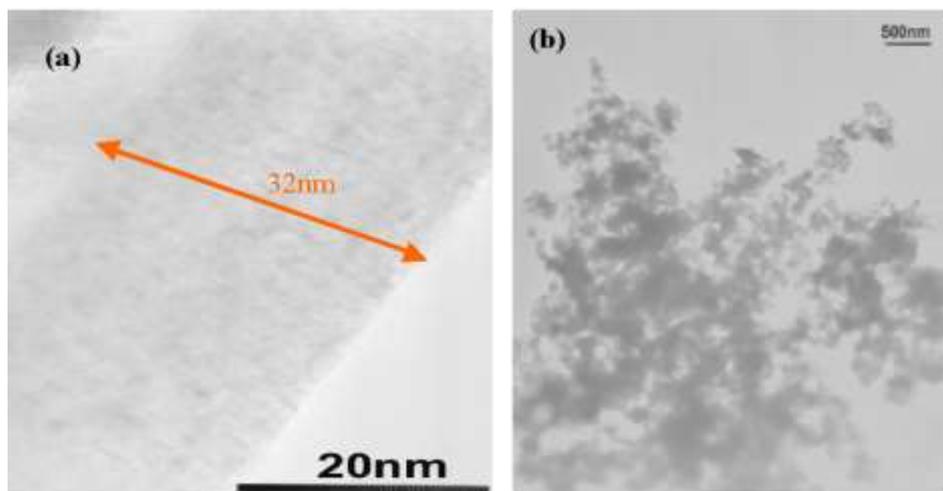
With increased sampling times the helicity and spirality of the microfibers increased, this can be attributed to the copious supply of carbon by direct disproportionation of CO on the metal surface, forming pentagonal and heptagonal carbon rings. The incorporation of a pentagon into a graphite layer produces an outer curvature, while the incorporation of a heptagon would produce an inner curvature [14]. Regular pairing of these pentagons and heptagons without any twist in the growth direction leads to spiral nanofibers as shown in Fig 10(a)



**Figure 10:** SEM image of (a) Spiral Microfiber. TEM image of (b) Helical Microfiber

Where as periodic pairing of pentagons and heptagons with a twist along the growth of the microfiber results in helical microfibers [14] as shown in Fig 10(b).

The TEM images of vertically aligned structures revealed that these structures are indeed bundles of micro tubes as shown in Fig 11. The outer diameter of the bundle was ~32nm. The bundle comprised of individual micro tubes, which might be either SWMT or MWMT (the nature of the tubes is not yet known as they could not be separated individually). The composition of the layer of catalyst particles at the tip of the tubes was found to be that of Ni-Cr. The size of the catalyst particles, as is evident from the TEM image, was in the range of 9-20nm.



**Figure 11:** (a) TEM image of a bundle of carbon micro tubes. (b) TEM image of Ni-Cr catalyst particles.

**Comparison of Vertically Aligned Nanostructures in Flames**

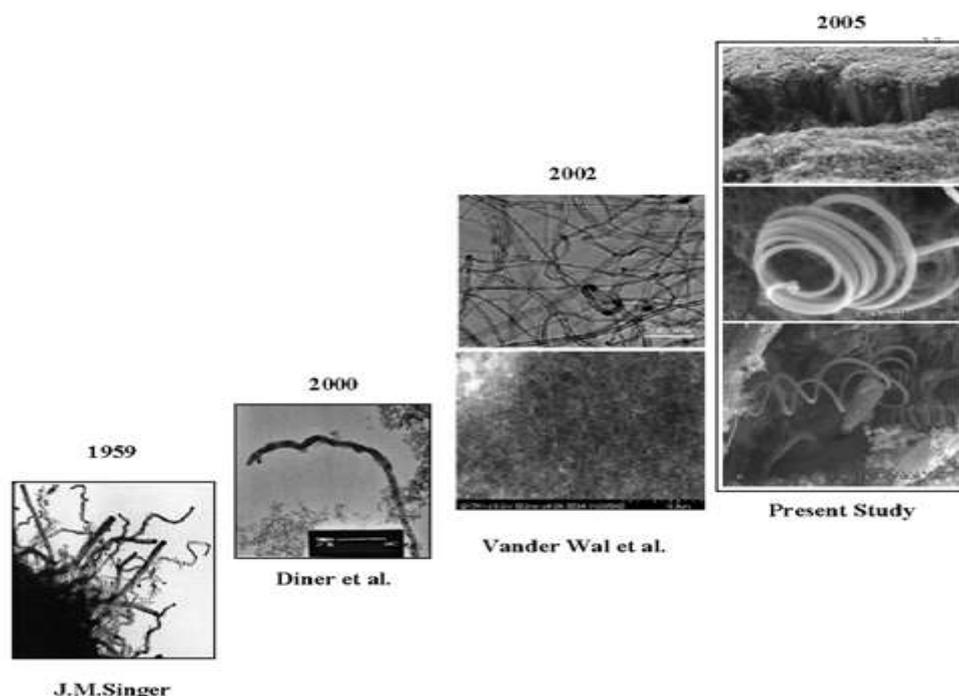
Aligned structures have been previously reported in diffusion flames but this is the first time that they are found in a premixed flame. A comparison of the aligned structures with those obtained in other studies is shown in Table.3

**Table 3: Comparison of Aligned Nanostructures**

Diffusion flame	Premixed flame	Diffusion flame
<ul style="list-style-type: none"> <li>&gt; Fusheng Xu et al [15].</li> <li>&gt; Methane Inverse Diffusion flame</li> <li>&gt; Ni/Cr/Fe (60%, 16%, 24%)</li> <li>&gt; MWNTs ~15-20nm</li> </ul>	<ul style="list-style-type: none"> <li>&gt; Present study</li> <li>&gt; Propane-oxygen Premixed flame</li> <li>&gt; 316 Stainless steel wire</li> <li>&gt; Compact bundles of CMTs.</li> </ul>	<ul style="list-style-type: none"> <li>&gt; Claudya P.Arana [16]</li> <li>&gt; Ethylene Diffusion Flame</li> <li>&gt; 302 Stainless steel wire (Fe/Cr/Ni)</li> <li>&gt; CNFs~0.5µm.</li> </ul>

A comparison of the present study with other premixed flame studies is shown in Fig.12. In 1959 J.M.Singer reported the growth of filamental structures in a premixed, eight percent propane-air flame. These filamental structures grown on steel grid are indeed MWNTs and nanofibers with lengths 1.5-5microns and diameters 49 – 470nm.

In 2000 Diener et al. reported the formation of MWNTs in benzene-oxygen and SWNTs in acetylene-oxygen flame with  $\phi$  ranging from 1.7-3.8 with the catalyst being nickelocene and ferrocene vapors.



In 2002 Vander Wal et al. conducted a series of experiments on the synthesis of carbon micro tubes in premixed flames, with ethane, ethylene, acetylene as the fuels and with cobalt coated stainless steel grid as the catalyst material and reported the optimal yield of MWNTs in premixed ethylene-air flame with  $\phi = 1.62$ .

#### IV. SUMMARY OF RESULTS

Carbon micro tubes and microfibers were produced using a premixed propane-oxygen flame with  $\phi$  ranging from 1.9 to 2.1. The effect of four catalysts Ni-grid, pure Ni-wire, Monel an alloy of Ni/Cu/Fe and Stainless steel wires on the structure and yield of the carbon microstructures was investigated. The diameter of these microstructures is strongly dependent upon the size of the catalyst particle. The diameter of the tubes increases with increasing catalyst particle size. MWMTs with diameters 27-40nm were observed with catalyst particle sizes 31-45nm, while CMFs with diameters ~125nm-500nm were observed with catalyst particle sizes 130-630nm. As the fuel equivalence ratio increased the diameters, lengths and the yield of the carbon microfibers decreased.

The carbon microstructures produced in the present study with Ni and Steel wires with optimum fuel equivalence ratio 1.9 are highly ordered in terms of helicity, spirality and vertical alignment. Also the vertically aligned microstructures appear as dense and consist of compact bundles of individual tubes, and are hollow in nature. Also a maximum yield of 2mg/min of carbon microfibers with Monel wire as the catalyst material was achieved.

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