Synthesis of carbon nanotubes by DC thermal plasma system

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Abstract: In order to synthesize carbon nanotubes (CNTs), an experiment was carried out with a discharge input power of 7~8 kW by a nitrogen thermal plasma. Micron-sized cobalt powder was used as a catalyst. Several limitations were observed in aspect to the size of catalyst nanoparticles. In order to overcome and successfully synthesize CNTs, high temperature characteristics were examined according to the operating conditions by a numerical analysis.

Keywords: DC thermal plasma, nitrogen, carbon nanotubes, numerical analysis

1. Introduction

Carbon nanomaterials are widely used in current industries, from fullerene to graphene and carbon nanotubes. Among them, CNTs are the hardest axial fibers ever created and are axially rolled up graphene. They have been applied as one of the transparent electrodes of flexible display touch panels, which are expected in the IT market because they can be bent and twisted like graphene. Also, the one-dimensional molecular structure with a large surface area and excellent mechanical (Elastic modulus: 1 TPa, Tensile Strength: 100 GPa), electrical, and thermal properties are able to widely apply in various industrial fields such as automotive parts, aviation, and semiconductors. CNTs have single-walled and multi-walled structures. Generally, in the same kind of metal or semiconductor products, single-walled carbon nanotubes (SWCNTs) have higher electrical conductivity than multi-walled carbon nanotubes (MWCNTs), whereas MWCNTs have higher mechanical strength and yield voltage than SWCNTs [1-4].

In general, CNTs are synthesized by sublimating and synthesizing a carbon material in an inert atmosphere of 3,900 K or more by chemical vapor deposition (CVD), laser ablation, flame synthesis method, and electric arc discharge [4]. Among them, thermal plasma, which is one of the arc discharge methods, has outstanding advantages such as unlimited phases of precursor (solid, liquid, gas phases), extremely high temperature (core temperature above 10,000 K), high energy density, and rapid condensation due to the sharp temperature gradient to synthesize nanomaterials [5]. In order to control the condensed product, several parameters are applied such as the flow rate of plasma-forming gas, the raw material injection rate, and input power, etc. They strongly influence reaction time, vaporization of raw materials, and quenching rate. The thermal plasma provides a higher temperature medium above the sublimation temperature of carbon, sublimated carbon elements are able to readily recompose to nanotube structures according to the operating conditions.

In this work, to synthesize CNTs by DC thermal plasma, the optimized synthesis conditions were determined through numerical analysis of the plasma torch using by Magnetohydrodynamic (MHD) code. Subsequently, synthesis experiments were performed in the optimized plasma medium.

2. Simulation Method

In order to solve the equation of mass, momentum, and energy conservation, it is assumed that the thermal plasma torch region is in a steady state and forms a two-dimensional axisymmetric. In addition, assuming that the thermal plasma jet is in a local thermal equilibrium (LTE) state, and a k-ε model (k: turbulence kinetic energy, ε: the rate of dissipation of turbulent kinetic energy) was applied to consider the turbulence of the thermal plasma flow.

The simulation domain of calculated torch was indicated in Fig. 1. Compared to conventional thermal plasma torch, the injection of raw material through a cathode nozzle is a unique feature in this plasma system. The numerical results were verified by comparison of calculated and measured voltages in Table 1. The errors between two values were approximately under 2%, which represented that the numerical analysis method used in this simulation was reliable.

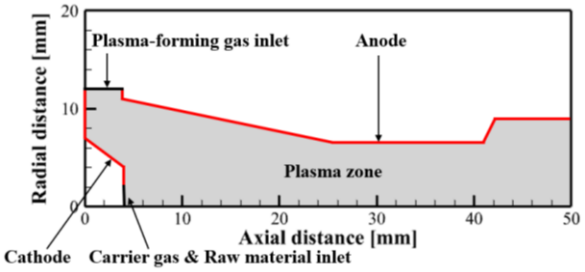

Fig. 1. Simulation domain of thermal plasma torch.

Table 1. Comparison of calculated and measured voltages.

-	Run 1	Run 2	Run 3
Ampere	30 A	50 A	70 A
Plasma gas	N_2		
Plasma gas flow rate	50 L/min		
Carrier gas flow rate	5 L/min		
Measured voltage	150 V	130 V	117 V
Calculated voltage	147 V	128 V	116 V
Error	2%	1.5%	0.9%

3. Experiments

The DC thermal plasma system consists of a power supply, a plasma torch, a powder injection device for metal catalyst, and a gas supply device for gases injection. The metal catalyst was introduced to the region between the torch nozzles through the hole in the cathode in Fig. 2, and

the reaction gases were injected as methane and hydrogen mixed gases into a reactor 1. In addition, a thermal insulation tube was inserted to expand the high-temperature area in the reactor.

The plasma-forming gas and carrier gas were used as 50 L/min and 5 L/min N_2, respectively. Cobalt micro-sized powder (Thermo scientific, 1.6 microns, 99.8%) was injected as a metal catalyst with 0.167 g/min feeding rate. The reaction gas was used as CH_4 (99.95% purity) and H_2 (99.999% purity) and the total flow rate was 2 L/min. the thermal plasma was discharged at 7~8 kW input power with 70 A.

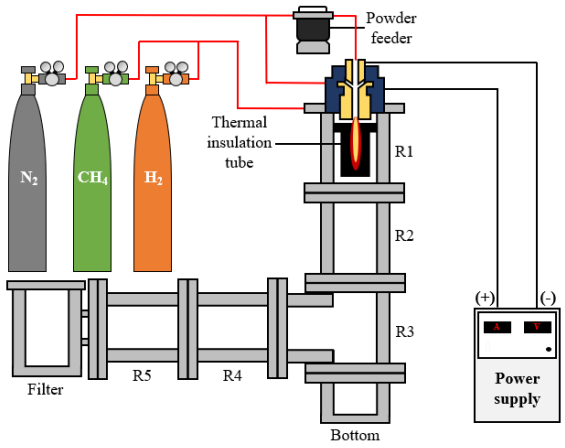

Fig. 2. Schematic diagram of DC thermal plasma system for carbon nanotubes synthesis.

4. Results & Discussion

Fig. 3 shows the temperature distribution in the torch inside at 7.7 kW (70 A). The highest temperature is about 6,000 K. The torch exit is at z = 104 mm, and the temperature is rapidly decrease to 1,000 K as it approaches the torch inner wall.

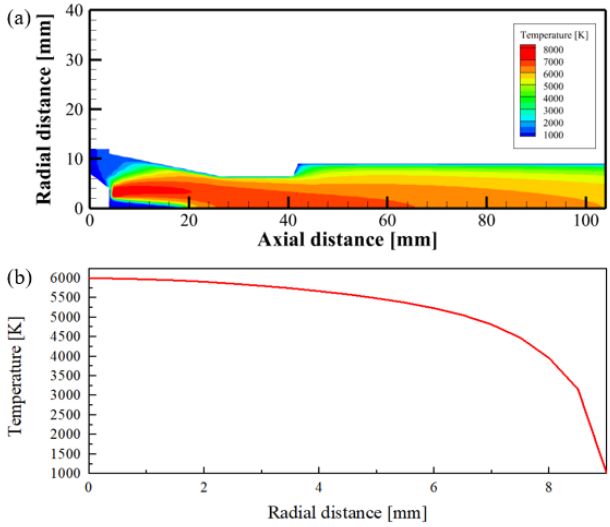

Fig. 3. (a) Temperature distribution inside the torch and (b) temperature profile at the torch exit at 70 A (Run 3).

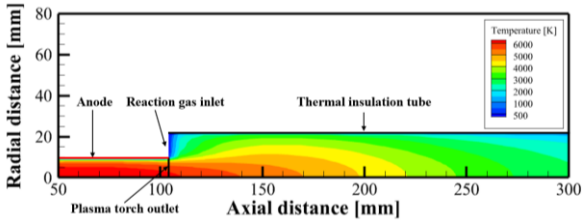

Fig. 4. Temperature distribution of the reactor with the thermal insulation tube at 70 A (Run 3).

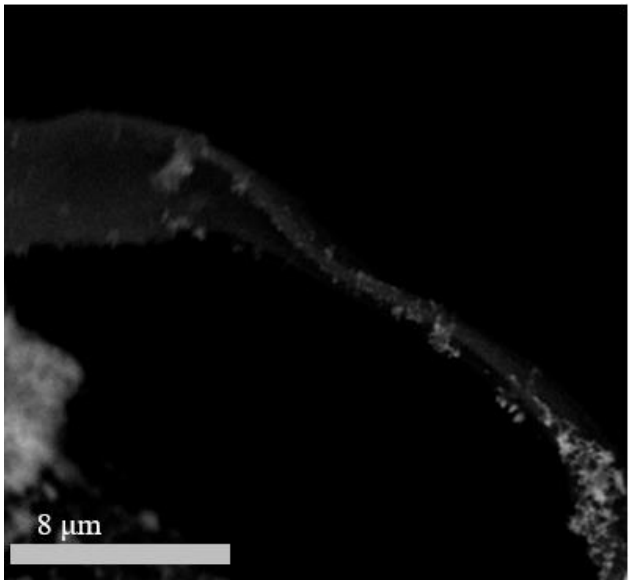

Fig. 5. SEM images of synthesized products collected in Reactor 2.

The high temperature environment was created above 2,000 K in Reactor 1 combined with the thermal insulation tube, and it is sufficient temperature for methane decomposition (1,120 K). Thus, it might be decomposed into hydrogen and carbon elements. The decomposed carbon sources were reacted with the metallic catalyst and grew on the surface of catalyst nanoparticles. The grown carbon materials were observed by SEM (Scanning Electron Microscope), and the texture of fiber was analyzed in Fig. 5. The fibers have larger sizes than typical CNTs. It seems to be strongly influenced the size and surface roughness of catalyst nanoparticles. Large-sized catalyst is not functioned as a growth medium of nanotubes. The thermal insulation tube for efficient decomposition of methane is able to be reduce the quenching rate of vaporized micron sized metal powder as the catalyst, and the size of metal catalyst is increased. Accordingly, it was discussed that decomposed carbon elements react with large catalyst particles and is synthesized into fibrous materials larger than nanotubes.

The temperature gradients in the thermal insulation tube were indicated in Fig. 6 according to the axial and radial distances. The cobalt has a vaporization temperature of 3,200 K and a melting temperature of 1,768 K. The temperature region above 3,200 K is relatively small and the temperature between 1,768 and 3,200 K is mostly

created inside the insulation tube. It leads to staying the catalyst in the droplet state, it has a negative influence to synthesize and grow to the nanotube morphology. To overcome this limitation and synthesize the CNTs, it requires that the expansion of temperature region allows catalyst vaporization or the reduction of residence time at the liquid state of the catalyst to prevent grain growth.

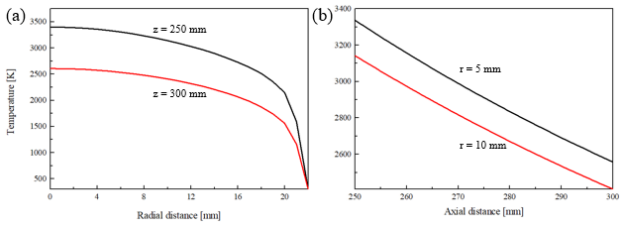

Fig. 6. Temperature profiles in the reactor according to the distances. (a) The radial distance is varied at the fixed axial distance, (b) the axial distance is varied at the radial distance.

5. Summary & Future plan

We performed CNTs synthesis experiment of Run 3 using a DC thermal plasma system. As a result, carbon fibers attached large metal catalyst particles were observed. It was discussed as a limitation for the long growth time of cobalt catalyst powder. In order to understand the relationship between the size of catalyst and products' texture, growth time of metal catalysts was controlled, whether a thermal insulation tube is present, and its length will be presented at the conference.

6. References

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