A New Type of Arc Plasma Reactor with Twelve-Phase Alternating Current Discharge for Synthesis of Carbon Nanotubes

Tsugio Matsuura, Keiji Taniguchi and Takayuki Watanabe
Industrial Technology Center of Fukui Prefecture, 61Kawai-Washizuka, Fukui, 910-0102, Japan
Professor Emeritus, Fukui University, 2-1302 Nakano, Fukui, 918-8186, Japan
Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8602, Japan

Abstract
A new type of arc plasma reactor with twelve-phase alternating current (AC) discharge for synthesis of carbon nanotubes (CNTs) is proposed. A couple of six discharge electrodes by which have mutually electrical connection between them to enlarge the high temperature regions in the reactor are arranged to three dimensional locations. A new method of CNTs fabrication by this reactor which accomplishes to enlarge the suitable growth region in high-purity and at high yield was developed.

Keywords Arc plasma, Twelve-phase AC discharge, Carbon nanotubes

1. Introduction

A large number of applications for arc plasma have been used for the welding and cutting of metals up to this time. Arc plasma as the energy source with effective heat efficiency has been also tried to open new technological field for better global environment with related new industrial markets, including plasma chemical reaction.

In general, the power source for generating arc plasma is accomplished by using a direct current (DC) power supply. This is the larger the capacity the higher the cost of apparatus for inverting from AC to DC. On the other hand, the single-phase and the three-phase AC power supply have already been proposed for the same application fields. Since these systems have a characteristic of intermittent discharge, the high power arc plasma systems generated by AC power supply have not been fully developed. In order to improve this defect, a multiple-phase AC power supply has been developed. To obtain a more effective arc plasma generator by expanding this concept, we have developed a twelve-phase AC power supply [1]. The most important advantage of this system is that there are large number of discharging paths among electrodes in comparison with the case of the single-phase and the three-phase systems. Therefore, some of the plasmas always exist for continuing smoothly the discharging action. It seems as if this system was driven by the DC power supply instead of actual commercial AC power supply (60 Hz) [2].

Since CNTs discovered in 1991 at first time [3], many researchers have been provided its unique physical and chemical properties, and applications to nano-scale devices. Several methods for synthesis of CNTs such as DC arc-discharge [3, 4], laser ablation and thermal chemical vapor deposition (CVD) have been presented. The DC arc-discharge method can synthesize CNTs in highest quality than the other methods mentioned above. However its yields are much lower. Up to date, CVD method is the mainstream of mass fabrication of CNTs. In order to avoid the disadvantage of the DC arc-discharge method, the twelve-phase AC arc-discharge method is proposed here. The purpose of this paper is to describe the techniques for obtaining its method and to show the experimental results for synthesizing CNTs by using this new type of arc plasma reactor.

2. Twelve-phase AC power supply for arc plasma reactor

2.1 Three-phase to twelve-phase conversion

Figure 1 shows the electrical circuit diagram of the transformers for converting from the three-phase AC to the twelve-phase AC and the schematic connection diagram of the plasma reactor. The input of the three-phase power supply is connected to 200V commercial power lines. The primary coils of transformers are divided into two parts: one is the Δ connection and the other is the Y connection. The twelve-phase power supply can be realized by the combination of these circuits. From the Y connection, the voltage components V_x, V_y, V_z, V_x', V_y', and V_z' of the six-phase AC are defined by the following equations:

$$V_i = V_m \sin(\omega t - \frac{n}{3}\pi), (i = x, y, z), (n = 0,2,4) \quad (1)$$

$$V_i' = V_m \sin(\omega t - \frac{n}{3}\pi), (i = x, y, z), (n = 1,3,5) \quad (2)$$

where V_m and f are the maximum value of the sinusoidal wave and the frequency of the AC (60 Hz), respectively.

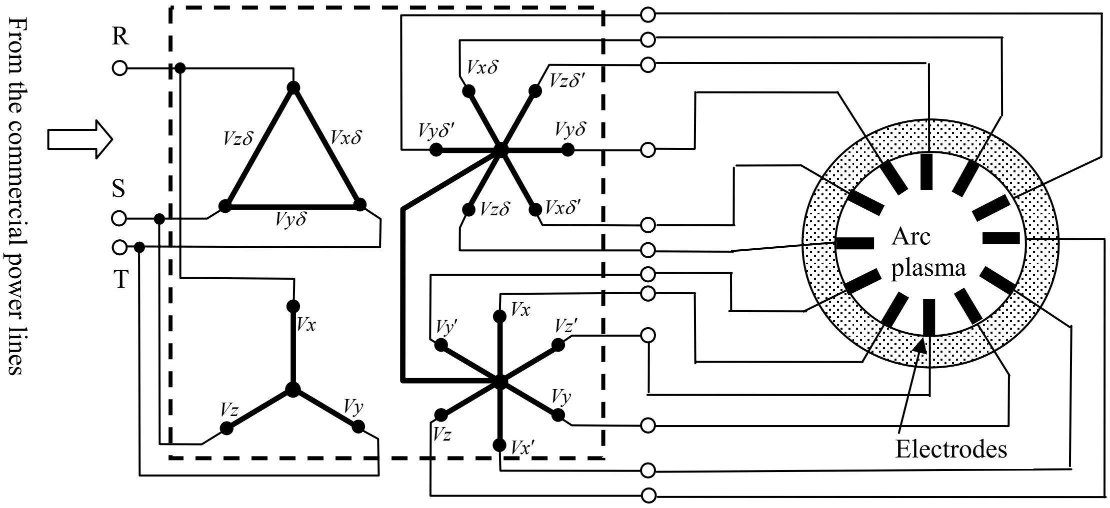


Fig. 1 Electrical circuit diagram and schematic temporary connection diagram of the plasma reactor

From the Δ connection, the voltage component $V_x\delta$, $V_y\delta$, $V_z\delta$, $V_x\delta'$, $V_y\delta'$, and $V_z\delta'$ are defined by the following equations:

$$V_i\delta = V_m \sin(\omega t - \frac{n}{6}\pi), (i = x, y, z), (n = 1,5,9) \quad (3)$$

$$V_i\delta' = V_m \sin(\omega t - \frac{n}{6}\pi), (i = x, y, z), (n = 7,11,15) \quad (4)$$

2.2 Advantages of the twelve-phase AC discharger

The configuration of twelve electrodes are symmetrically arranged to bring out the advantages of the twelve-phase discharge. The geometrical arrangement of the tips of electrodes is indicated in Fig. 2. In the case of the distance between electrodes No.5 and No.7 is unity, the ratio of the distance among other electrodes have the values as shown in the same figure.

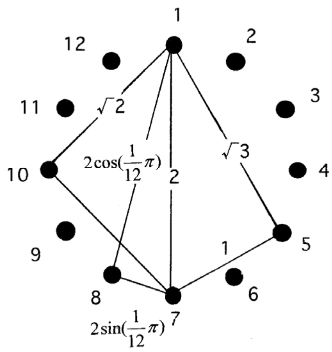


Fig. 2 The geometrical arrangement of the tip of electrodes

In general, the voltage applied between each electrodes and neutral point of the secondary coil of the transformer for the twelve-phase AC power supply can be described by following equation.

$$V_i = V_m \sin(\omega t - \frac{(i-1)}{6}\pi), (i = 1.....12) \quad (5)$$

From this equation, we can obtain the difference of the voltage between the electrode No.1 and the others. These are explained as follows:

$$V_2 - V_1 = 2\sin(\frac{1}{12}\pi)V_m \cos(\omega t + \frac{1}{12}\pi) \quad (6)$$

$$V_3 - V_1 = V_m \cos(\omega t + \frac{1}{6}\pi) \quad (7)$$

$$V_4 - V_1 = \sqrt{2}V_m \cos(\omega t + \frac{1}{4}\pi) \quad (8)$$

$$V_5 - V_1 = \sqrt{3}V_m \cos(\omega t + \frac{1}{3}\pi) \quad (9)$$

$$V_6 - V_1 = 2\cos(\frac{1}{12}\pi)V_m \cos(\omega t + \frac{5}{12}\pi) \quad (10)$$

$$V_7 - V_1 = 2V_m \cos(\omega t + \frac{1}{2}\pi) \quad (11)$$

Here we should notice that the ratio of the voltage amplitudes in equations (6)-(11) is equal to the ratio of the geometrical distances shown in Fig. 2. As the phase shift is kept constant every moment by the combination of transformers, the values of voltage/distance among each electrode are also constant every moment.

2.3 Power supply for the twelve-phase AC discharge

To realize the power supply for the generation of twelve-phase AC discharge, twelve pieces of single-phase AC arc welding transformer (DAIHEN B-250) were used. These welders are the conventional ones and have a dropping characteristic. The input voltage, the maximum non-loading output voltage, the typical loading voltage, the wattage and the range of output currents are 200 V, 80 V, 32.5 V, 12.4 kW and from 75 A to 250 A, respectively. Two pairs of six transformers are connected to the commercial AC line (three-phase 200 V, 60 Hz) with the figures of Δ and Y connections. Twelve output lines from the transformers are directly connected to the corresponding electrodes of the reactor.

Fig. 3 Setup of the twelve-phase AC power supply

Fig. 4 Photograph of the twelve-phase AC arc discharge

Fig. 3 shows the setup of the twelve-phase AC power supply. The picture of the twelve-phase AC arc discharge is shown in Fig. 4. Typical voltage and current waveforms of the single-phase AC arc discharge and the twelve-phase ones are shown in Fig. 5 and Fig. 6, respectively.

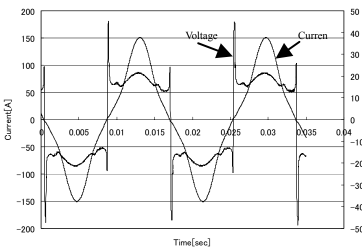


Fig. 5 Voltage and current waveforms in case of single -phase AC

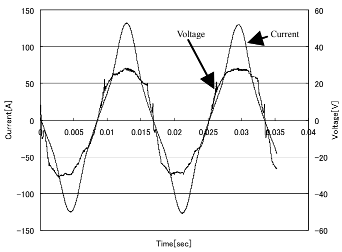


Fig. 6 Voltage and current waveforms in case of twelve-phase AC

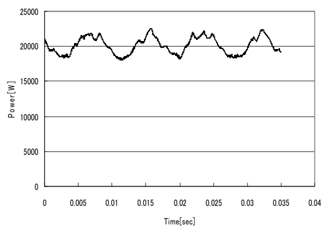


Fig. 7 Total power waveform in case of twelve-phase AC

Fig. 6 indicates the twelve-phase AC arc discharges which do not have an intermittent discharge. The waveform of the total power in the case of twelve-phase is also shown in Fig. 7. The ripple of the total power was 6.3%.

3. Synthesis of carbon nanotubes

3.1 A new type of arc plasma reactor

A new type of arc plasma reactor with twelve-phase AC discharge for mass fabrication of CNTs is shown in Fig. 8. The CNTs were produced by a twelve-phase AC arc discharge among carbon electrodes in helium gas. The electrodes of graphite rod 12mm in diameter, 500mm in length having the purity of 99.995% are configured horizontally in the reactor as shown in Fig.4. Since the electrodes are consumed by evaporation, the arc gaps among electrodes are kept constant by the motor-drive systems of which are adjusted by the voltage among them.

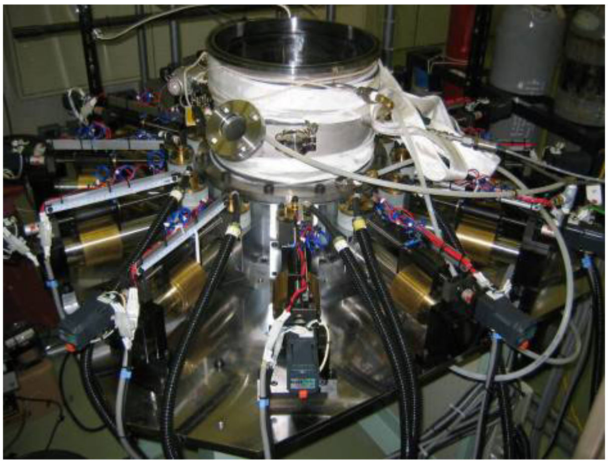


Fig. 8 A new type of arc plasma reactor for mass fabrication of CNTs

3.2 Experimental setup

Figure 9 shows the schematic diagram of the experimental setup inside of the reactor. The substrate made of the stainless steel plate (sus304, 50 mm in width, 320 mm in length and 1 mm in thickness) suspended from the ceiling of the reactor. The tip of the substrate was apart 10 mm above from the center of twelve electrodes configuration. The diameter of the plasma surrounded by the tips of twelve electrodes is approximately 60 mm.

After purging in the chamber, helium gas (purity 99.99%) is introduced and sets at 600 torr. The discharging voltage and its current are 20-45 V and 70-100 A, respectively. The carbon electrodes contain nickels as the catalyst for CNTs synthesis at 10wt. %.

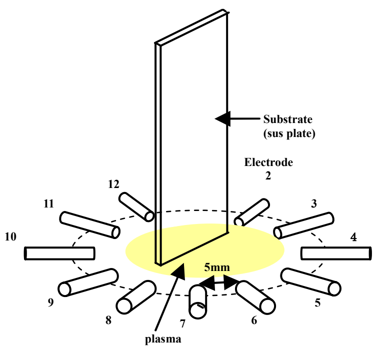


Fig. 9 Schematic diagram of the experimental setup inside the reactor

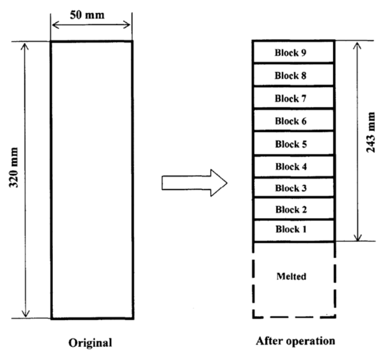


Fig. 10 Substrate for CNT deposition (original and after operation)

3.3 Experimental results and discussion

The CNTs synthesis is strongly related to the temperature of condensation and growth of carbon molecules in plasma [5, 6], therefore the deposition was carefully analyzed to investigate the effect of deposition temperature. During the discharge for one hour, CNTs were prepared from the evaporation of the electrodes. A lot of soot-like deposit was obtained on the surface of the substrate as well as on the inner surface of the reactor. Figure 10 shows the original substrate and after operation one. The surface of remained substrate was divided equally into nine blocks. The deposit on the substrate is carefully gathered from nine sampling blocks. The products were examined using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy with a 514.5nm Ar^{+} laser and were also characterized by using an energy dispersive X-ray analysis (EDX)

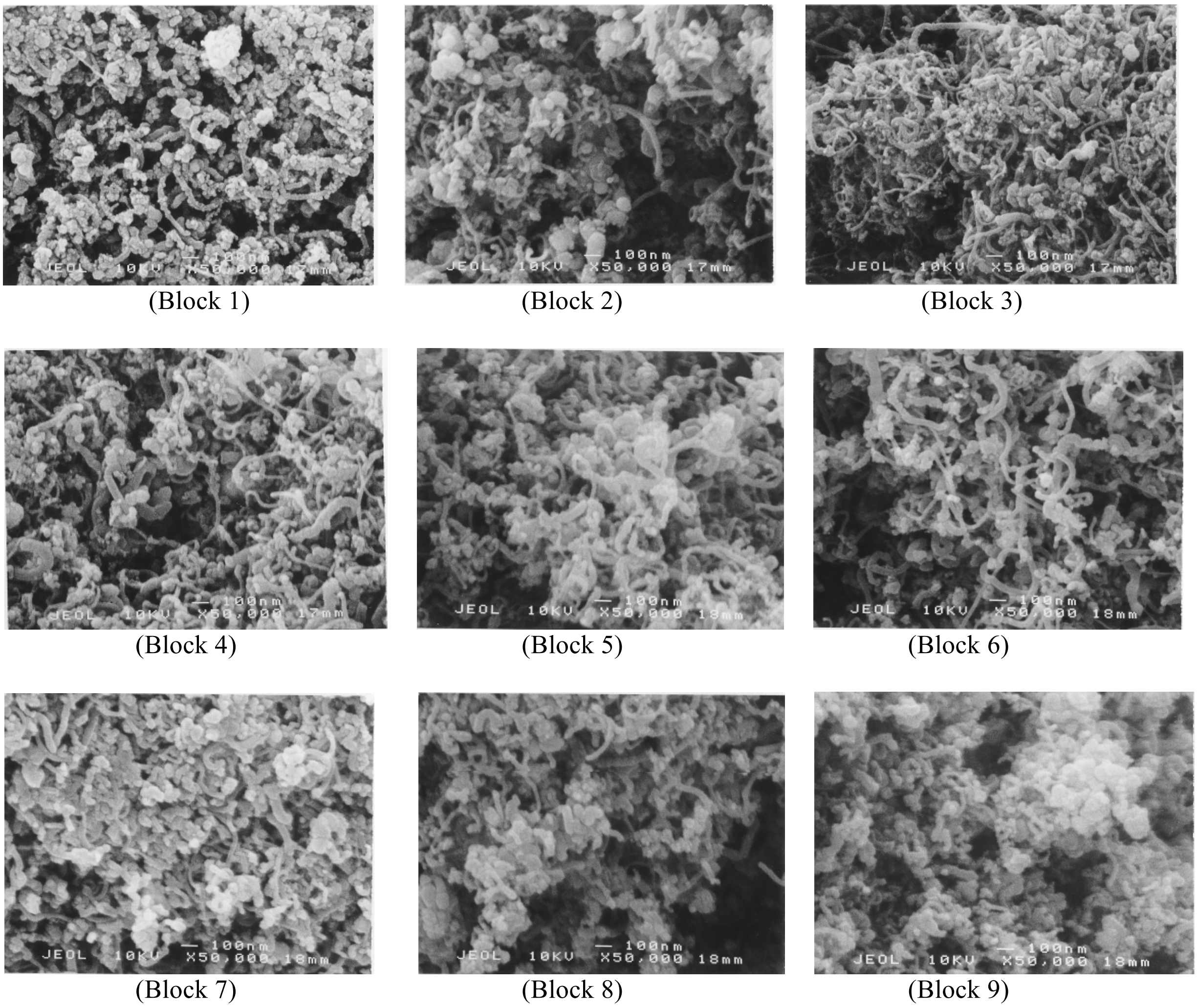


Fig. 11 SEM images of the CNTs from gathering nine blocks on the substrate

The SEM images of crude samples at each block of the substrate are shown in Fig.11. The clusters of carbon particles which are considered to be amorphous carbons are much more observed at the images of blocks 1, 2, 7, 8, and 9 in comparison with the images of blocks 3-6. On the contrary, CNTs with much less amorphous carbons are observed at the images of blocks 3-6. The surface temperature at the tip of block 1 of the substrate is estimated at 1400 degree Celsius of its melting point. The surface temperature of the bottom of block 9 was measured at 800 degree Celsius by using the thermocouples. From these evaluations, the temperature distribution on the substrate can be roughly estimated with the linear assumption of the temperature distribution. The optimum temperature for CNTs synthesis is approximately in the range from 1000 to 1250 degree Celsius. This result was congruous well with previous report [7]. From the morphological observation of blocks 2 and 8, even though their locations are not suitable for fabrication of CNTs, the length of it in block 8 is shorter than that of block 2. The multi-walled CNTs of 20 nm-40 nm in diameter shown in Fig. 12 were produced not only on the substrate but also on the wall of reactor. Nickel particle filled with the CNTs shown in Fig. 13 was identified by the energy dispersive X-ray spectrometry.

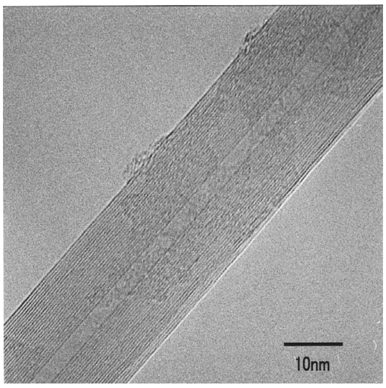


Fig. 12 TEM image of the multi wall CNTs

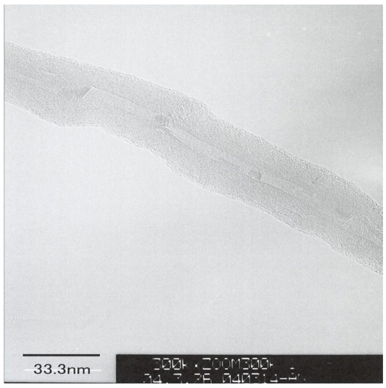
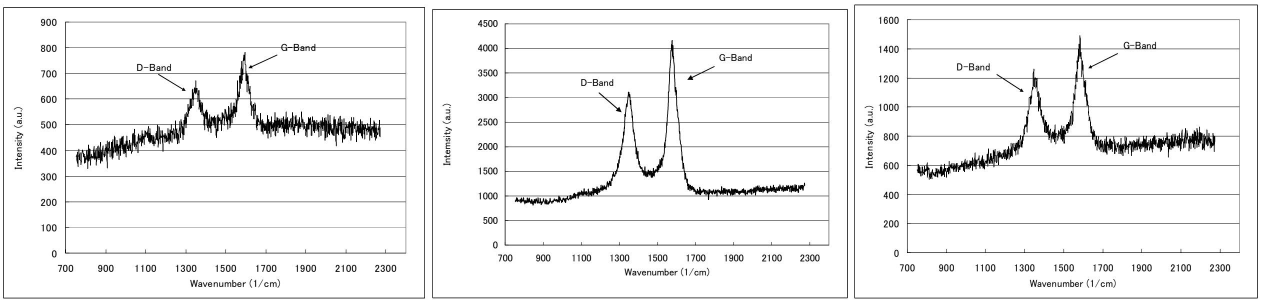


Fig. 13 CNTs filled with nickel particles

Raman spectrum shown in Fig. 14 contains the G-band (1580 cm^{-1}) and the D-band (1360 cm^{-1}). In general, the G-band shows the CNT oriented peak and the D-band shows the amorphous carbon or the structure defects of CNTs oriented peak. The synthesis of CNTs is not clearly found out on the block 1 shown in Fig.14 (a). Fig.14 (c) shows CNTs and the amorphous carbon are both synthesized on the block 8. On the contrary, the strong peak of G-band caused by synthesis of CNTs was appeared on the block 6 shown in Fig.14 (b). These results were congruous very much with the morphological observation of SEM images mentioned above.



(a) block 1 (b) block 6 (c) block 8

Fig. 14 Raman spectrum of the CNTs on the substrate

4. Conclusions

We have described the techniques for obtaining the new type of arc plasma reactor with twelve-phase AC discharger. This configuration can provide the attractive advantages of the arc plasma in superior stability and long continuity. A new method of CNTs fabrication by using this reactor which accomplishes to enlarge the suitable growth region in high-purity and at high yield was developed. The optimum temperature for CNTs synthesis is approximately in the range from 1000 to 1250 degree Celsius. The multi-walled CNTs of 20 nm-40 nm in diameter were produced

5. References

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