Experimental and Numerical Studies of Heat Convection in the Synthesis of Single-Walled Carbon Nanotubes by Arc Vaporization

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Abstract

Numerical analysis on heat convection in the synthesis of single-walled carbon nanotubes (SWNTs) by arc vaporization is carried out to calculate the cooling rate of carbon clusters and the temperature distribution of the buffer gas (helium) during the synthesis. The effects of three factors, gravity ($G = 1, 2$, and $3 g_0$, where $1 g_0$ is normal earth gravity), input power ($P = 500, 1000, 2000$, and 3000 W), and buffer gas pressure ($p = 40, 50, 80$, and 100 kPa) are investigated. By comparing the calculated results with those of a previous synthesis experiment under gravity conditions of $G = 1, 2$, and $3 g_0$, it is clarified that differences in the cooling rate and the shape of the high-temperature region of the buffer gas cause considerable changes in both the yield and quality of SWNTs produced. The similarity of the heat convection under different input powers and buffer gas pressures is also considered.

1. Introduction

When single-walled carbon nanotubes (SWNTs)¹⁾ are synthesized by arc vaporization, various factors, including the type and pressure of the buffer gas and the amount of metallic catalyst included in the carbon anode, affect the yield, quality and type of carbon clusters produced. Heat convection is also thought to affect the production of SWNTs. Mieno^{2, 3)} reported that heat convection affects the synthesis of such carbon clusters upon carrying out a synthesis experiment under a repetitive micro-gravity environment, using a vertically swinging vessel and parabolic flights⁴⁾.

To study the effects of heat convection on the synthesis of SWNTs, first, we carried out synthesis experiment⁵⁾ involving arc vaporization under the normal gravity condition ($G = 1 g_0$) and high-gravity conditions ($G = 2$ and $3 g_0$), and numerical calculations of heat convection under the same gravity conditions. Then, the experimental results are compared with the calculation results. A fluid calculation code (SMAC method,⁶⁾ Fuji Research Institute α -Flow) is used to calculate the distribution of the gas temperature, the heat convection velocity, and the cooling rate of helium gas around the arc plasma. Calculations of the effects of input power and buffer gas pressure are also carried out to study the similarity among the heat convection for different gravity conditions, input powers, and buffer gas pressures.

2. Experimental Procedure and Results

Figure 1(a) shows a schematic of the reaction device. The vacuum chamber is made from 4-mm-thick stainless steel, has a 160 mm internal diameter, and is 200 mm high. An anode “a” with a cross section of $6 \times 6 \text{ mm}^2$ and made of Ni-Y-doped graphite, and a cylindrical graphite cathode “b”, 8 mm in diameter, are set at the center of the

chamber. A carbon cluster collector “c”, made up of 16 copper cylinders, each of which is 1 mm thick, 8 mm in inner diameter, and 20 mm long, is set at $x = 10$ mm, $y = 0$ mm to collect carbon clusters.

The anode is sublimated by DC arc discharge of current $I_d = 45$ A in helium gas of pressure $p = 50$ kPa. The carbon clusters are collected at $z = 0, 10, 20, 30, 40, 50, 60, 70,$ and 100 mm. These carbon cluster samples are analyzed using a Raman spectrometer (JASCO NR-1800, triple monochrome Raman spectrometer, Ar laser, $\lambda = 532$ nm, power = 70 mW). The same reaction device is used for the experiments under three different gravity conditions ($G = 1, 2,$ and $3 g_0$). The experiments under $G = 2$ and $3 g_0$ are carried out using the rotating accelerating generator of JAXA (Tsukuba Space Center, Japan).^{7, 8)} The discharge time is 7 min for each gravity condition.

The experimental results under different gravity conditions are compared and some significant differences are confirmed.⁵⁾

(a) Lower soot yield is found under the high-gravity conditions. The total yields of soot by 7 min production under the three gravity conditions of $G = 1, 2,$ and $3 g_0$ are 64.1, 26.7, and 35.5 mg, respectively.

(b) Under $1 g_0$, SWNTs with diameters from 1.32 to 1.52 nm are detected by the Raman spectrometer. Under $3 g_0$, the diameter of SWNTs is uniform and 1.55 nm. Under $2 g_0$, the diameter of SWNTs is 1.46 or 1.55 nm as shown in Fig. 2.

(c) Large increase in the G/D ratio in the Raman spectra is confirmed for a limited part of the samples under $3 g_0$ as shown in Fig. 3.

(d) Decrease in the volume of the region in which SWNTs are synthesized is confirmed as the gravity increases to $3 g_0$.

From these findings, it is conjectured that under the higher-gravity conditions, the synthesis region becomes smaller, but more effective synthesis of SWNTs takes place in this region.

3. Numerical Calculation Method

Figure 1(b) shows the boundary conditions of the calculation. The dimensions of the cylindrical shape are those of the actual chamber. A cylindrical heat source (8.8 mm in diameter, 8.8 mm high) with a heating rate of 1.89×10^9 W (corresponding to an input power of 1000 W) is set as the arc plasma source at the center of the chamber. The inner wall, top, and bottom surface temperatures of the cylinder are fixed at 400 K. The region labeled by symbols A - F is specified as the calculation region, which is divided into 18×46 cells, in which the noncompression fluid model is solved under suitable boundary conditions. The cylindrical coordinate system is used in this calculation.

This calculation is based on two assumptions: (1) the buffer gas (helium) can penetrate into the heat source, and (2) the temperatures of carbon molecules and metallic particles are the same as that of the buffer gas. Hence, the calculation of the temperature variations of the buffer gas can be approximated by those of the carbon molecules and metallic particles.

In this numerical analysis the gas temperature (T_{gas}), the gas velocity (V_z), and the cooling rate of the buffer gas are calculated for $t = 0 - 10$ s. The cooling rate C_i is defined as:

$$C_i = \frac{T_{gas i} - T_{gas i+1}}{t} \quad (1)$$

$$t = \frac{0.0044}{V_{zi+1} + V_{zi}} \times 2 \quad (2)$$

where “ i ” is the number of cells , “ t ” is the time needed for one carbon particle to move from one cell to the next one, “0.0044 ” is the size of the cell in m.

4. Comparison between Calculated and Experimental Results

4.1 Numerical calculation of heat convection under different gravity conditions

Figures 4(a) - 4(c) show images of the calculated temperature (500 - 8000 K) distributions of the buffer gas for $G = 1, 2$, and $3 g_0$, respectively. Figures 5(a) - 5(c) are images of the calculated velocity vectors of molecules of buffer gas for $G = 1, 2$, and $3 g_0$, respectively. Figure 4 shows that the hot gas region decreases in volume as the gravity increases. Figure 5 shows that as the gravity increases the heat convection becomes stronger and the swirl caused by the heat convection also becomes stronger and shifts upward. After about 4 s the heat convection becomes stable.

Figure 6 shows the vertical variation of the calculated gas temperature (T_{gas}) at $x = 11$ mm, $z = 0 - 100$ mm, and $t = 10$ s. It is clear that T_{gas} decreases as the gravity increases. The decrease in the soot yield under high-gravity conditions is conjectured to be caused by the decrease of the temperature, which suppress the sublimation of the carbon electrode.

The experimental results show that the synthesis region of SWNTs decreases under the high-gravity condition, as Fig. 3 shows that SWNTs are found on the cluster collector from $z = 0$ to 60 mm for $1 g_0$, and from $z = 10$ to 40 mm for $2 g_0$ and $3 g_0$. Here an assumption is made that SWNTs can be synthesized only above 2500 K (dotted line in Fig. 6). Then the synthesis region for $1 g_0$ is $z = 0 - 65$ mm, the synthesis region should be about $z = 0 - 50$ mm, and $z = 0 - 40$ mm for 2 and $3 g_0$, respectively.

Figure 7(a) shows the variation of the calculated velocity (V_z) of the buffer gas at $x = 11$ mm, $z = 0 - 100$ mm, and $t = 10$ s. V_z increases and the peak value of V_z shifts upward as the gravity increases. Figure 7(b) shows the variation of the calculated cooling rate of the buffer gas at $x = 11$ mm, $z = 0 - 100$ mm, and $t = 10$ s. The cooling rate increases as the gravity increases, and the largest cooling rate appears at $z = 15$ mm for $1 g_0$ and at $z = 20$ mm for 2 and $3 g_0$. The variation of cooling rate corresponds to that of V_z : the higher the gas velocity, the higher the cooling rate becomes.

The strong swirl under the high-gravity condition is thought to affect the synthesis of SWNTs. The strong swirl in the upper part of the chamber (in Fig. 5) can maintain the clusters in the upper part of the chamber, where the conditions are suitable for the SWNT growth. Thus, these clusters have a longer reaction time. And this corresponds to the improvement of the G/D ratio under the high-gravity condition.

4.2 Numerical calculations of heat convection under different input powers

Numerical calculations for $P = 500, 1000, 2000$, and 3000 W, $p = 50$ kPa, and $G = 1 g_0$, are carried out to study the change in the heat convection at different input powers. Figure 8 shows that the volume of the high-temperature region increases significantly as input power increases. For $P = 2000$ and 3000 W the distribution of the high-temperature region is almost hemispherical. Figure 9 shows that for $P = 2000$ and 3000 W the heat convection forms two swirls, one in the upper part and one in the lower part of the chamber. Figure 10 shows that T_{gas} increases as the input power increases. According to the calculated results for the effects of gravity and the experimental results, SWNTs appear to be produced above about 2500 K under condition of $p = 50$ kPa and $G = 1 g_0$ as shown in Fig. 6. Thus, it can be expected that

SWNTs can be synthesized at $z = 0 - 20$ mm when $P = 500$ W, $z = 0 - 65$ mm when $P = 1000$ W, $z = 0 - 75$ mm when $P = 2000$ W, and $z = 0 - 80$ mm when $P = 3000$ W (as shown in Fig. 10 by the dotted lines). Because of the hemispherical distribution of the high-temperature region under $P = 2000$ and 3000 W, which is similar to that under $0 g_0$,⁴⁾ the SWNTs are considered to be synthesized over a wider region in the chamber.

Figure 11(a) shows the variation of V_z for the buffer gas at $x = 11$ mm, $z = 0 - 100$ mm, and $t = 10$ s for different input powers. Large differences in V_z among the different input powers can be found. In particular, for $P = 2000$ and 3000 W, the velocity of the gas is very low. Figure 11(b) shows that the calculated cooling rates of the buffer gas for $P = 2000$ and 3000 W are much lower than those for $P = 500$ and 1000 W. Therefore, longer reaction time is obtained at the high input power.

4.3 Numerical calculations of heat convection under different gas pressures

Figure 12 shows images of the calculated gas temperature distributions under different pressures ($p = 40 - 100$ kPa, $P = 1000$ W, $G = 1 g_0$). The volume of the high-temperature region decreases as pressure increases. Figure 13 shows images of the calculated velocity vector of the heat convection. The trends in the change in the volume of the high-temperature region and the vector image of heat convection are similar to those under the high-gravity conditions.

Figure 14 shows that T_{gas} at $x = 11$ mm, $z = 0 - 100$ mm, and $t = 10$ s decreases as gas pressure increases and that the temperature variation along the z -coordinate becomes smaller as the gas pressure increases. Figure 15(a) shows the calculated variation of the velocity (V_z) of the buffer gas at $x = 11$ mm, $z = 0 - 100$ mm, and $t = 10$ s, and Fig. 15(b) shows the calculated cooling rate of the buffer gas. V_z for the buffer gas

increases and the average cooling rate of the buffer gas decreases as the pressure increases. Also, the curves of the cooling rate for high gas pressures are very flat, meaning that under high gas pressures, the temperature distribution is more even than that under the lower gas pressures.

5. Discussion and Conclusions

Numerical calculations are carried out to determine the effects of gravity, input power, and buffer gas pressure on heat convection to the gas temperature and the cooling rate. The effects of gravity on heat convection in the synthesis of SWNTs are studied by comparing the experimental and the calculated results under $G = 1, 2$, and $3 g_0$. Under the high-gravity conditions, decrease of the volume of synthesis region of SWNTs, growth of the swirl, and the high buffer-gas cooling rate are confirmed, which would improve the G/D ratio and the uniformity of SWNTs.

According to the calculation results, under the high input power, the distribution of the high-temperature region is similar to that under the weak gravity condition, and the volume of the region in which SWNTs are synthesized may be significantly larger. On the other hand, under the high gas pressure, the volume of the high-temperature region is smaller and its distribution is similar to that under the high-gravity condition. Thus, the region in which SWNTs are synthesized is conjectured to decrease in volume as the gas pressure increases.

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References

- 1) H. Dai: in *Carbon Nanotubes* ed. M. S. Dresselhaus, G. Dresselhaus, and Ph. Avouris (Springer, New York. 2000) p. 30.
- 2) T. Mieno: New Diamond Front. Carbon Technol. **16** (2006) 139.
- 3) T. Mieno: Plasma Phys. Control. Fusion **46** (2004) 211.
- 4) T. Mieno and M. Takeguchi: J. Appl. Phys. **99** (2006) 104301.
- 5) G. Tan and T. Mieno: to be published in Thin Solid Film (2009).
- 6) R. Peyret and T. D. Taylor: *Computational Methods for Fluid Flow* (Springer, New York, 1983) p. 160.
- 7) G. Tan and T. Mieno: Proc. Int. Conf. Asia MRS (IUMRS-ICA 2008), 2008, RP-10.
- 8) G. Tan and T. Mieno: Proc. 2nd Int. Conf. Plasma-Nano Technology and Science (IC-PLANTS 2009), 2009, P-10.

Figure Captions

Fig. 1. (a) Schematic of the reaction device. The center of the chamber was set as the origin of the coordinates. A cluster collector is set at $x = 10$ mm. “a” and “b” denote the carbon electrodes and “c” denotes the cluster collector. (b) Boundary conditions of the numerical calculation. The input power of the heat source is 1000 W.

Fig. 2. Distribution of the diameters of SWNTs for gravity conditions of $G = 1, 2$, and $3 g_0$. The sizes of SWNTs are highly uniform under $3 g_0$ and vary under $1 g_0$.⁵⁾

Fig. 3. Raman spectra of the carbon samples for two gravity conditions. (a) G and D bands for $1 g_0$. (b) G and D bands for $3 g_0$. A significant increase in G/D ratio can be confirmed under $3 g_0$ (quoted from ref. 5).

Fig. 4. (Color print) Calculated profiles of the distribution of the buffer gas temperature (T_{gas}) for 1, 2, and $3 g_0$. $t = 0.25 - 4.0$ s, $p = 50$ kPa, $P = 1000$ W.

Fig. 5. Calculated vector images of the heat convection for 1, 2, and $3 g_0$. $t = 0.25 - 4.0$ s, $p = 50$ kPa, $P = 1000$ W. Arrows under the graphs show the magnitude of the velocity.

Fig. 6. Calculated buffer gas temperature T_{gas} vs z-coordinate for $G = 1, 2$, and $3 g_0$. $x = 11.0$ mm, $y = 0$ mm, $z = 0 - 100$ mm, $t = 10.0$ s, $p = 50$ kPa, $P = 1000$ W.

Fig. 7. (a) Calculated V_z for the buffer gas vs z-coordinate and (b) calculated cooling rate of the buffer gas vs z-coordinate for 1, 2, and $3 g_0$. $x = 11.0$ mm, $y = 0$ mm, $z = 0 - 100$ mm, $t = 10.0$ s, $p = 50$ kPa, $P = 1000$ W.

Fig. 8. (Color print) Calculated profiles of distributions of the buffer gas temperature for $P = 500, 1000, 2000$, and 3000 W. $t = 10.0$ s, $p = 50$ kPa, $G = 1 g_0$.

Fig. 9. Calculated vector images of the heat convection for $P = 500, 1000, 2000$, and

3000 W. $G = 1 g_0$, $p = 50$ kPa, $t = 10.0$ s.

Fig. 10. Calculated buffer gas temperature T_{gas} vs z-coordinate for $P = 500, 1000, 2000$ and 3000 W. $t = 10.0$ s, $p = 50$ kPa, $G = 1 g_0$, $x = 11.0$ mm, $y = 0$ mm, $z = 0 - 100$ mm.

Fig. 11. (a) Calculated V_z for the buffer gas vs z-coordinate. (b) Calculated cooling rate of the buffer gas vs z-coordinate for $P = 500, 1000, 2000$, and 3000 W. $t = 10.0$ s, $p = 50$ kPa, $G = 1 g_0$, $x = 11.0$ mm, $y = 0$ mm, $z = 0 - 100$ mm.

Fig. 12. (Color print) Calculated profiles of the buffer gas temperatures (T_{gas}) for four gas pressures $p = 40, 50, 80$, and 100 kPa. $G = 1 g_0$, $t = 10.0$ s, $T_{gas} = 500$ K - 8000 K.

Fig. 13. Calculated vector images of heat convections for 4 gas pressures: $p = 40, 50, 80$, and 100 kPa. $G = 1 g_0$, $P = 1000$ W, $t = 10.0$ s.

Fig. 14. Calculated buffer gas temperature T_{gas} vs z-coordinate, $t = 10.0$ s, $G = 1 g_0$, $P = 1000$ W, $p = 40, 50, 80$, and 100 kPa. $x = 11.0$ mm, $y = 0$ mm, $z = 0 - 100$ mm.

Fig. 15. (a) Calculated V_z for the buffer gas vs z-coordinate. (b) Calculated cooling rate of the buffer gas vs z-coordinate. $t = 10.0$ s, $G = 1 g_0$, $P = 1000$ W, $p = 40, 50, 80$, and 100 kPa. $x = 11.0$ mm, $y = 0$ mm, $z = 0 - 100$ mm.

Fig. 1

Fig. 2

(a) $1g_0$

(b) $3g_0$

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12

Fig. 13

Fig. 14

Fig. 15