Characterization of Carbon Nanofibers Synthesized by Using the Well-Controlled Thermal Plasmas

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A continuous synthesis technique to produce carbon nanofibers(CNFs) including multi-walled carbon nanotubes (MWNTs) is studied by using the forced constricted type plasma jet generator. In this method, CNFs production using catalyst powders (Ni, Fe) is more enhanced compared to that using only CH_4/H_2 gas mixtures. The length of the CNFs on the substrate has been increased with increasing the process time. Prepared CNFs using Fe powders are more improved in quality than that using Ni powders.

KEYWORDS: thermal plasma processing, plasma jet, carbon nanofibers, catalyst powders (Ni, Fe)

1. Introduction

Thermal plasma processing using a plasma jet with a high speed and a high heat capacity is one of the most promising methods for synthesizing new materials. We have developed the well-controlled thermal plasma reactor based on the forced constricted-type plasma jet generator. The reactor can produce a plasma jet with high stability and high thermal efficiency for various operating conditions [1]. So far, we have reported the rapid synthesis of ferrite particles from powder mixtures [2] and diamond films from CH_4/H_2 gas mixtures [3] using this reactor with relatively low power operation.

Recently, much attention has been paid to carbon nanofibers(CNFs) including carbon nanotubes (CNTs). They are characterized by some of physical and structural properties. Especially, CNFs have interesting characteristics, namely, thermal conductivity, electric conductivity, and mighty mechanical intensity, etc. [4]. In general, arc discharge, laser ablation and chemical vapor deposition (CVD) methods have been mainly used for preparation of CNFs [5-7]. CNFs prepared by the arc discharge method have higher crystallinity and a lower number of defects than those prepared by CVD [8]. But, at the same time, diameters of CNFs produced by the arc discharge method are distributed in a wide range. In addition, arc discharge method is basically not a continuous but a discontinuous process. Thus, the production method with low cost, high quality and continuous synthesis is required now.

To this end, we have studied application feasibility of the well-controlled thermal plasma reactor for synthesis of CNFs. Until now, CNFs can be produced using CH_4 gas as material gas and H_2 gas as assist gas [9,10]

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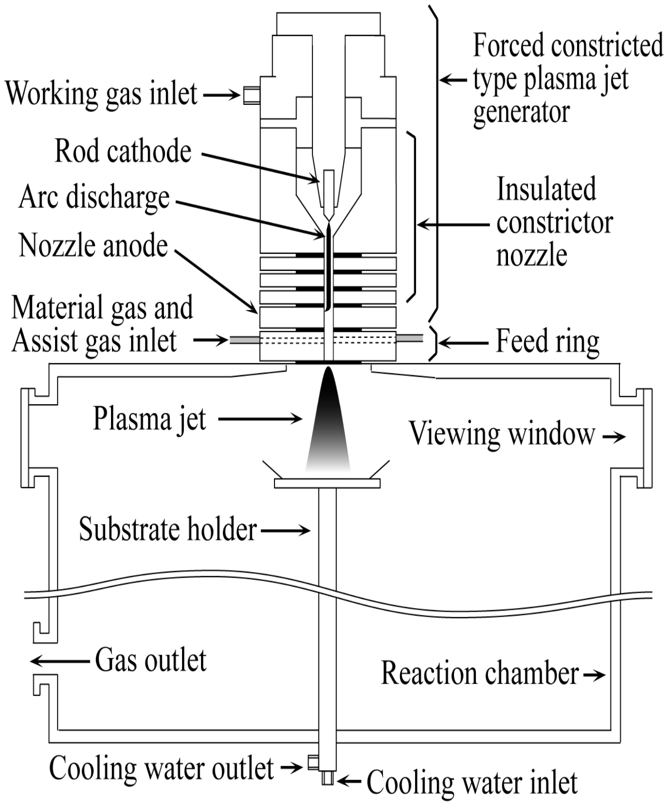


Fig.1. Schematic diagram of thermal plasma reactor with plasma jet system.

In addition, injecting Ni catalyst powders, production of CNFs has been well enhanced. Moreover, it is confirmed that synthesis of CNFs is mainly caused by surface process on the substrate [11].

In this paper, we further study the effect of catalyst powders (i.e. Ni and Fe) for CNFs synthesis. To clarify further the surface reaction, relationship processing duration times and growth of CNFs are studied. At the same time, quality of the synthesized nanoclusters is also characterized.

2. Experimental set-up and procedure

The well-controlled thermal plasmas reactor is shown in Fig.1 [12]. The reactor consists of the forced constricted-type plasma jet generator, the feed ring, the reaction chamber and the substrate holder. The plasma jet is produced by dc arc discharge with working gas Ar. As the insulated constrictor nozzle is set between the nozzle anode and the cathode, arc length is always kept constant and the nozzle wall strongly constricts the arc with the working gas. Then, a stable plasma jet with high heat capacity is produced under various operating conditions. CH_4 gas, H_2 gas and catalyst powders are injected into the plasma flow of high-temperature region directly through two capillary feeding ports of the feed ring. The produced materials are collected on the substrate. The substrate is set on the substrate holder in Fig.1.

Typically, experiments have been performed under the following conditions: jet power (W_j) is 5 kW; the distance from the feed ring exit to substrate position (L) is 60 mm; the pressure (P_t) in the reaction chamber is 760 Torr; the working gas (Ar) flow rate (Q_w) is 20 l/min; material gas (CH_4) flow rate (Q_m) is 0.3 l/min; assist gas (H_2) flow rate (Q_a) is 8 l/min and processing duration time (T) is 10 min.

In this experiment, the substrate material is sus430. Characterization of prepared products is done by the scanning electron microscope (SEM), TEM and Raman spectrometer etc.

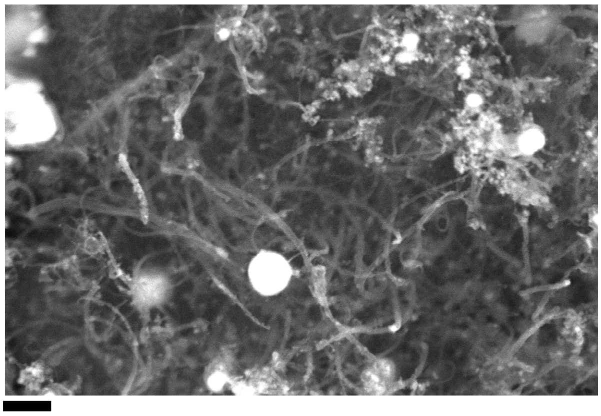
3. Experimental results and discussion

According to the previous results [11], it is confirmed that production of CNFs is well enhanced by injecting Ni powders compared with that by using only CH_4/H_2 gas mixtures, and that CNFs production is mainly caused by surface reaction.

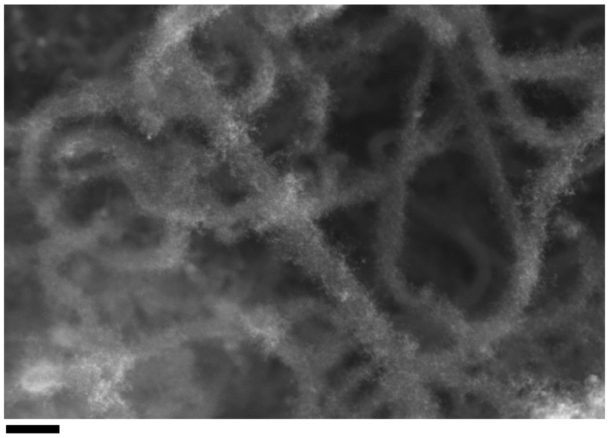
In this paper, the effect of catalyst powders on CNFs synthesis is further studied. At first, syntheses using Fe powders, using Ni powders and without powders are done. The reason to use the Fe powders is that generally the acid treatment [13] of Fe powders is easier than that of Ni powders. Moreover Ni powders are toxic substance. Then, human body may be damaged if Ni powder goes into the inside of the body.

Synthesis procedure is as follows [11]: At first, assist gas (H_2), material gas (CH_4) and powders are injected at the same time into a plasma jet. After 30 seconds past, only powders injection is stopped and injection of CH_4/H_2 gases is continued. Total processing duration time is 10 min. Powders flow rate Q_f is 0.02 g/min. The particle size of the Fe powder is 35μm and that of the Ni powder is 40μm.

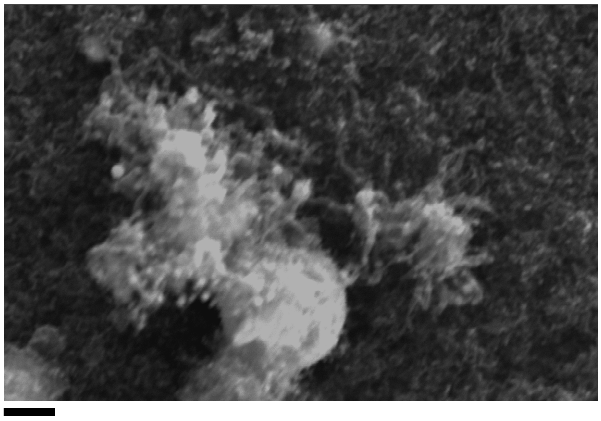
Figure.2 shows the SEM images of products prepared on the substrates. As is shown clearly, in both cases (a) and (b), it is confirmed that CNFs have been synthesized. But for case (c), CNFs are slightly synthesized. In addition, diameter of CNFs in (a) is smaller than that of (b). However, the length of CNFs is nearly equal with each other.



1μm (a) with Fe powders



1μm (b) with Ni powders



1μm (c) without powders

Fig.2 SEM images of products prepared on substrate (sus430). Preparation conditions are as follows: W_j = 5 kW, P_t = 760 Torr, Q_w = 20 l/min, Q_m = 0.3 l/min, Q_a = 8 l/min, T = 10 min, T_f = 30 s, Q_f = 0.02 g/min, L = 60 mm.

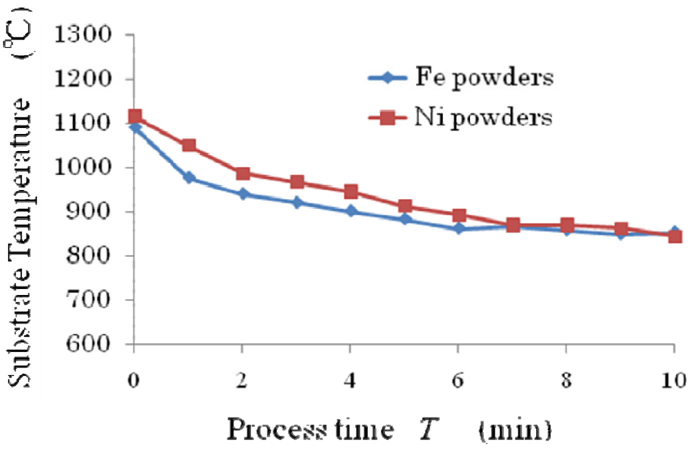


Fig.3. Substrate temperature by an increase of time, corresponding to Fig 2

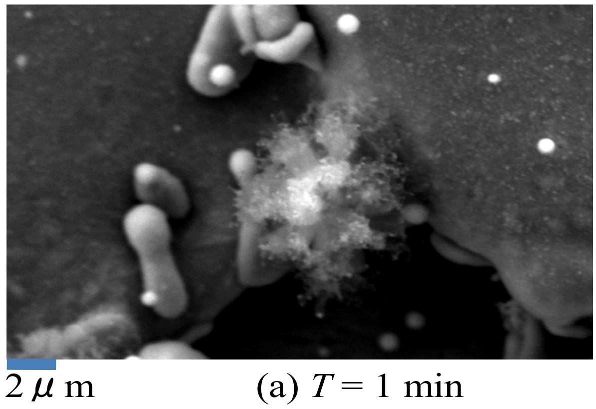
Next, the surface temperature of the substrate is measured with a radiation thermometer. Time dependence of temperature on the substrate surface is shown in Fig 3. Temperature difference between two cases is not so large although there is some difference in the early period. Then, the surface condition on CNFs synthesis is nearly the same between the case (a) and (b).

Relationship between processing duration times and growth of CNFs are studied. The SEM images of products prepared with using Fe powders are shown in Fig.4, where process time is 1 min in (a), 4 min in (b), 7 min in (c) and 10 min in (d). Comparing (a) with (b), the length of CNFs which has been observed in (b) is longer than that in (a). In addition, the length of CNFs is increased with process duration time, and the longest CNFs can be confirmed in (d). Thus the CNFs like a long fibroid string have been grown with increasing the process time. In another experiment, we also confirm that the CNFs production depends strongly on the substrate temperature. These are further evidences that CNFs production is mainly caused by surface process

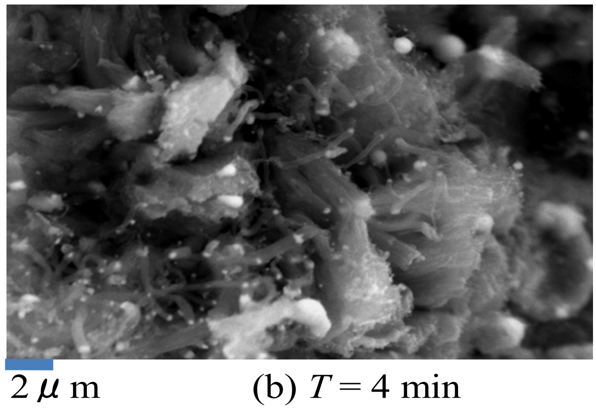
Finally, the quality of synthesized CNFs is estimated with Raman spectroscopy. The result is shown in Fig 5, (a) with Fe powders, and (b) with Ni powders. When the CNFs are synthesized, clear peaks of D-band and G-band are observed. Generally, qualities are also improved with increasing the ratio G-band/D-band. The ratio G/D in (a) is larger than that in (b). Thus prepared CNFs in (a) has more high quality than that in (b).

4. Summary

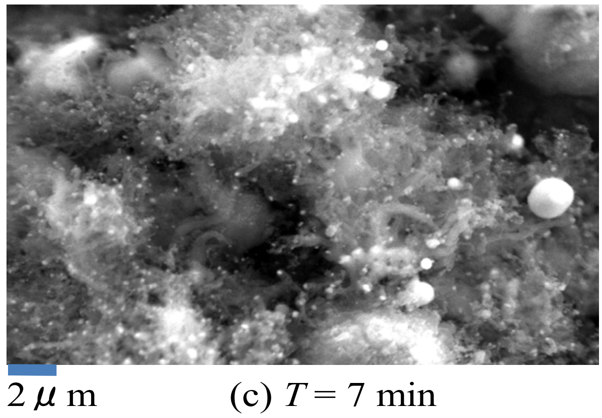
In this paper, we further study the effect of powders (Ni and Fe) on CNFs synthesis. For both cases, it is confirmed that CNFs production is enhanced compared with that using only CH_4/H_2 gas mixtures. According to the experimental procedure, it is confirmed that synthesis of CNFs, is caused mainly by surface reaction, the length of the CNFs on the substrate has been increased with increasing the process time. The quality



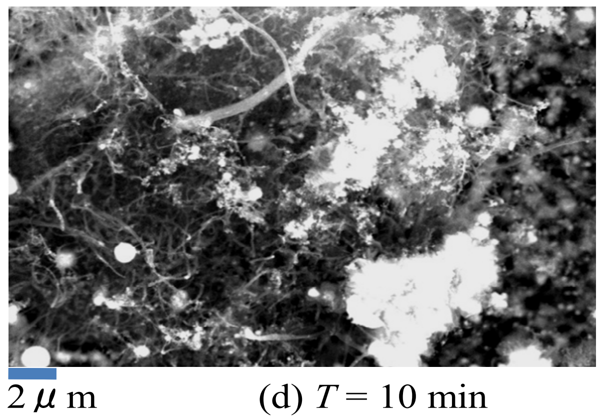
(a) T = 1 min



(b) T = 4 min

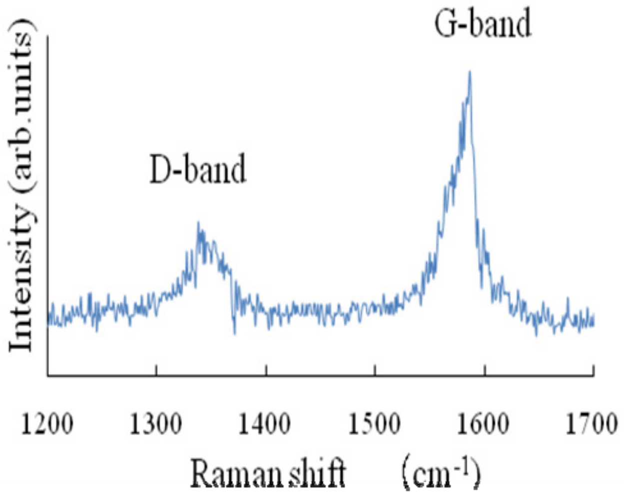


(c) T = 7 min

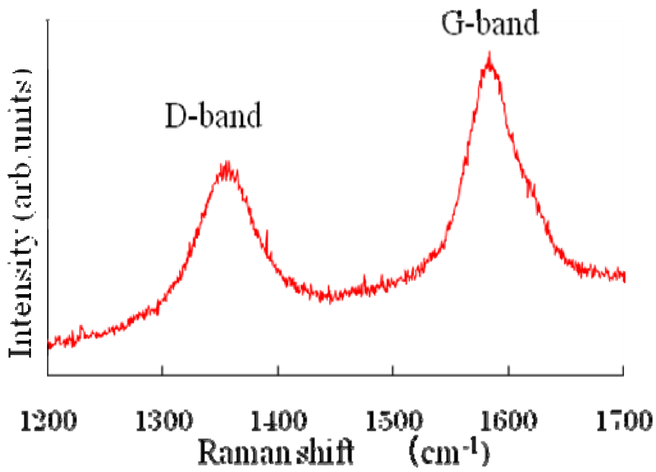


(d) T = 10 min

Fig.4 SEM images of products prepared on the substrate using Fe powders for four different process times. Preparation conditions are as follows: W_j = 5 kW, P_t = 760 Torr, Q_w = 20 l/min, Q_m =



(a) With Fe powders



(b) With Ni powders

Fig.5 Raman spectra of prepared carbon nanofibers prepared on substrate (sus430). Preparation conditions are as follows: W_j = 5 kW, P_t = 760 Torr, Q_w = 20 l/min, Q_m = 0.3 l/min, Q_a = 8 l/min, T = 10 min, T_f = 30 s, Q_f = 0.02 g/min, L = 60 mm.

of synthesized CNFs is estimated with Raman spectroscopy. Since the ratio G/D band in CNFs using Fe powders is larger than that using Ni powders, CNFs using Fe powders have higher quality than that using Ni powders.

In the future, for enhancement of CNFs synthesis including quality, effect of the substrate temperature should be discussed in detail.

5. Acknowledgements

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