

Plasma Treatment of Carbon Nano-powder Using RF Dielectric Barrier Discharge at Atmospheric Pressure

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A plasma processing apparatus for powdery material has been developed using a RF dielectric barrier discharge (DBD) with a gap below 1 mm at atmospheric pressure. By employing a 13.56 MHz frequency, the DBD power density was increased to more than 5 W/cm² even when confined in a small gap. Large floccules consisting of nano-size carbon particles were broken to smaller sizes using a RF-DBD apparatus with a small amount of O₂ in Ar at atmospheric pressure. It was demonstrated that the RF-DBD plasma apparatus operating at atmospheric pressure was useful for continuous plasma treatment of powdery material.

Key words: atmospheric pressure glow (APG) plasma, dielectric barrier discharge (DBD), RF, powder

1. INTRODUCTION

Atmospheric pressure glow (APG) plasma is getting a lot of the attention these days[1-5]. Desktop-sized plasma processing apparatus with no vacuum system will soon be possible through the use of APG plasma.

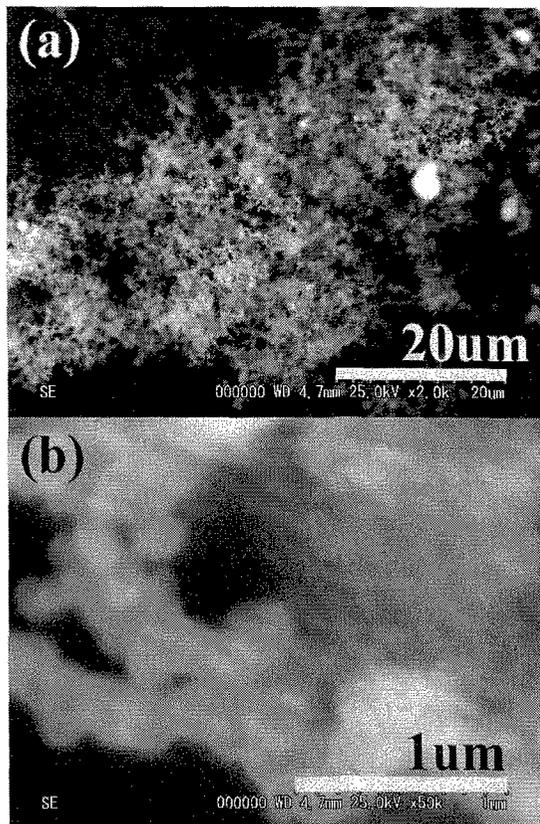


Fig.1 SEM images of the nano-carbon powder as (a) fibrous structures at lower magnification and (b) connected spherical particles at higher magnification.

One of the advantages of APG plasma is the ease of conveying powdery material continuously with a higher-pressure gas flow than with conventional plasma.

At atmospheric pressure, however, the discharge current should be limited to avoid arcing through the use of pulse modulation (PM) and/or dielectric barrier discharges (DBD). The time averaged power density of PM and DBD, using conventional frequencies such as several 10 kHz, was small due to the current limits. In this study, an RF of 13.56 MHz was used for DBD to increase the power density for a variety of plasma processing. Even at higher frequencies, a dielectric barrier was still effective to avoid arcing.

Carbon nano-powder was used to test the RF-DBD apparatus. The carbon nano-powder was soot-like flakes made through thermal decomposition of wasted polyethylene-terephthalate (PET) in a non-oxidizing atmosphere. By SEM observation at a lower magnification, the powder flake has fibrous structures as shown in Fig.1(a). At a higher magnification, as shown in Fig.1(b), the fiber appears to be made of spherical particles of 100 to 200 nm in diameter. Fig.2 shows the Raman spectra for the carbon nano-powder. The Raman spectra shows the G- and D-peaks, which are usually characteristic for amorphous graphite.

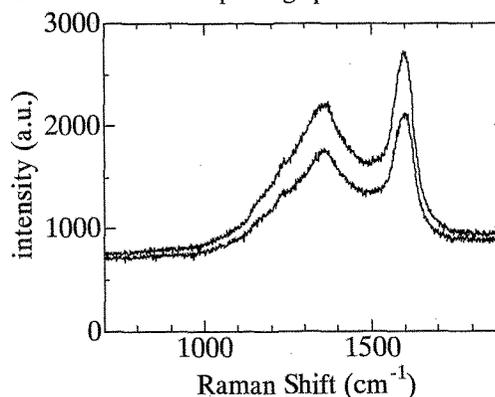


Fig.2 Raman spectra for the carbon nano-powder.

Though the material has not yet been fully characterized, it is interesting to find a novel recyclable application of the waste material. The 100 to 200 nm diameter carbon nano-particles aggregated to form flakes as large as 100 μm . If the flakes can be dispersed to their original size, it may be of use as spherical carbon nano-powder.

In this paper, we demonstrated the applicability of the RF-DBD plasma for continuous treatment of powdery material. The plasma was tested in order to separate the carbon fine particles by partial oxidization using a RF-DBD plasma apparatus.

2. EXPERIMENTAL

2.1 Experimental apparatus

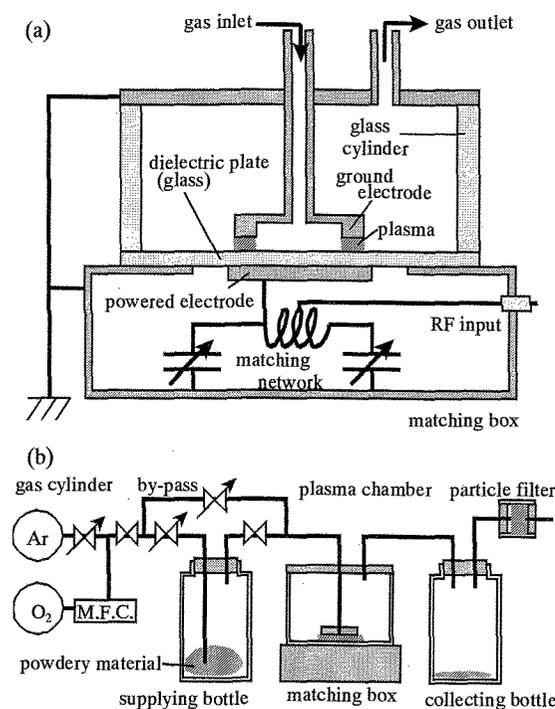


Fig.3 Experimental apparatus for RF-DBD at atmospheric pressure. (a) Plasma chamber and electrodes, and (b) gas line for powder supplying and recovery.

A schematic drawing of the plasma chamber using the RF-DBD at atmospheric pressure is shown in Fig.3(a). The RF powered electrode of the Cu disk was attached to the dielectric plate (glass) placed on the top face of the RF matching box. The grounded electrode was supported on the dielectric plate with a small gap. The gap length between the dielectric plate and the grounded electrode could be changed from 10 to 1,000 μm . In this experiment, it was fixed at 400 μm .

The grounded electrode, made of SUS, was ring-shaped and had a 30 mm outer diameter, a 20 mm inner diameter, a 5 mm ring width, and a total area of 4 cm^2 . The plasma cell was placed in a closed chamber that consisted of a glass tube and a top plate of SUS. Discharge gas and powdery material were introduced into the gap through the tube connected to the center of the grounded electrode, flown through the gap, and finally drained through the tube connected to the top

plate.

A schematic drawing of the gas piping and powdery material is shown in Fig.3(b). Ar gas was supplied through a needle valve with monitoring the flow rate. A small amount of oxygen was mixed to the Ar through a mass flow controller. The Ar flow rate was 1 to 5 slm and O₂ flow rate was 10 sccm. The O₂ concentration in the gas was varied from 0.2 to 1 %.

The original carbon powder, stored in the supplying bottle, was inserted in the upstream of the plasma chamber. After the treatment, the powder was collected in a bottle connected to the downstream portion of the plasma chamber. The carrier gas of Ar with O₂ was fed into the supplying bottle through a nozzle to agitate the original carbon powder. The powder sustained in the gas was carried continuously into the plasma chamber together with the gas flow.

Changing the ratio of the flow rates through the supplying bottle and the by-pass line controlled the supplying rate of the powder. After the plasma treatment, larger particles were deposited on the bottom of the bottle when the carrier gas resided in the collecting bottle.

The smaller particles in the gas line were caught by a 10 μm mesh filter. The filtered gas was dispensed directly to the atmosphere. The fine particles smaller than the filter mesh were also exhausted to air. The pressure in the plasma chamber was slightly higher than the atmospheric pressure due to conductance in the piping and in the terminating filter.

2.2 Experimental conditions

RF-DBD plasma was operated for plasma treatment of the carbon powder using a pure Ar or Ar/O₂ mixture gas. Because it was necessary to increase the gas flow rate to more than 1 slm in order to agitate the carbon powder, the Ar flow rate was changed from 1 to 5 slm while the oxygen flow rate remained constant at a 10 sccm, the maximum rate used in the experiment.

The plasma was sustained with a 20 W RF power. The RF power density input into the plasma was 5 W/cm^2 , even if using such a small gap. From the gas flow rates and the cross-section of the plasma region, the residence time of the gas in the plasma was estimated as several ms.

Optical emission spectroscopy of the plasma was carried out through the wall of the glass chamber using a multi-channel spectrometer. The emission spectra from the plasma with and without the carbon powder then were compared.

3. RESULTS AND DISCUSSION

The carbon powder was transported together in the

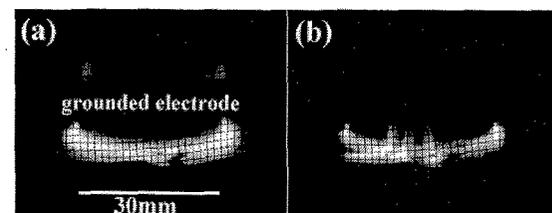


Fig.4 photographs of the plasma (a) without and (b) with the carbon powder.

gas flow in order to check the powder supplying system. The powder was continuously supplied to the plasma chamber and was collected in the recovery bottle. The powder was deposited mostly on the bottom of the recovery bottle when the plasma was not in operation. The supply rate was about 1 mg/min at a typical gas flow rate of several slm.

Fig.4(a) and (b) are photographs of the plasma with and without the carbon powder, respectively. Without the powder, the plasma appeared uniform along with the ring shaped electrode. The dark grid patterns are due to a RF shielding wire mesh enclosing the plasma chamber. Although the thickness of the plasma was 400 μm , it looked thicker due to the reflection from the dielectric glass plate.

As the carbon powder was introduced, spots of intensive emission rapidly moving in the plasma appeared. These emission spots appeared with the carbon powder both in the pure Ar plasma and Ar/O₂ plasma. The emission was caused by heated particles in the plasma. The flakes of carbon particles were heated not only by the plasma but also by inductive current in the conductive material induced by the RF field.

The plasma optical emission spectra are shown in Fig.5. With pure Ar, there were some sharp lines that originated from Ar atoms ranging from 700 to 850 nm and a weak continuously broadened band of emission centered at 550nm.

The intense sharp line of around 308 nm was possibly due to OH radical dissociated from water vapor emitted from the dielectric plate, because its intensity was not always reproducible but was also affected by the experimental procedure. The intensity of 308 nm peak gradually decreased along with discharge time.

The 777 nm peak emission, originated from O atoms, appeared in the pure Ar plasma spectrum also due to the contaminated water vapor. When a small amount of oxygen was added, the continuous band intensity decreased while the 777 nm line intensity increased.

After supplying carbon powder into the plasma, emission peaks for CH and C₂ appeared in the visible range. These results suggested that the carbon particles were partially decomposed by the plasma treatment and that the original powder contained hydrogen along with carbon.

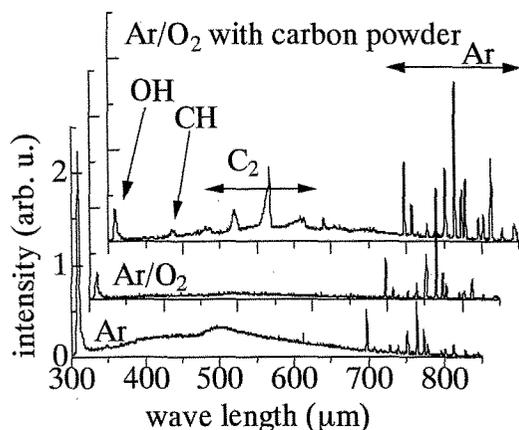


Fig.5 Optical emission spectra from the plasma of Ar, Ar with O₂, and Ar/O₂ with the carbon powder.

After the pure Ar plasma treatment, the powder was deposited mostly on the bottom of the collecting bottle and was slightly caught in the filter. The pure Ar plasma treatment was not effective for decreasing the coagulation size of the carbon particles.

By incorporating a small amount of oxygen into Ar, the collection of powder in the bottle diminished. After the Ar/O₂ plasma treatment, the powder passed through the collecting bottle and stopped in the particle filter or leaked out into the air. The Ar/O₂ plasma treatment was effective in breaking the large coagulated flakes into smaller ones.

At a O₂ concentration of more than 1 % (1 slm of Ar with 10 sccm of O₂), there were carbon powder combustions even after exiting the plasma region. The burning of the carbon powder was not controllable by the plasma condition. The carbon powder was almost entirely burned out and was recovered neither in the collecting bottle nor in the particle filter.

At the oxygen concentration of 0.2, 0.3, and 0.5 % (2, 3, and 5 slm of Ar with 10 sccm of O₂), the carbon powder was mostly recovered in the terminating filter. Fig.6 (a) and (b) show the SEM images of coagulated flakes of carbon particles before and after the Ar/O₂ plasma treatment. The size of the coagulated flakes was almost 100 μm in the original powder and was almost 10 μm after the plasma treatment. Even if the flakes could be broken down smaller than 10 μm , they would pass through the filter into the air due to the filter size.

The large coagulated flakes of carbon were broken into smaller ones by the plasma treatment with only a

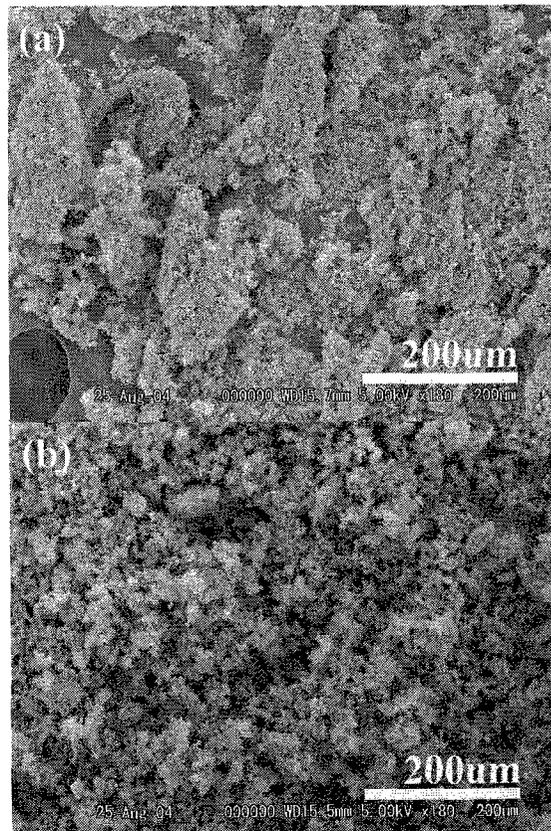


Fig.6 SEM images of coagulated flakes of carbon powder (a) before and (b) after the Ar/O₂ plasma treatment.

small amount of O₂ added to the Ar. The pulverization of the coagulated flakes was due to partial etching of the connection between the fine particles. However, the size of the collected powder was still larger than the original size of the particles. Some powder possibly decomposed to the original size and could not be collected by the present experimental setup. It is necessary to recover the smaller particles after the plasma treatment by bubbling the gas in a solvent.

It was demonstrated that the RF barrier discharge plasma at atmospheric pressure was useful for continuous plasma treatment of powdery material.

4. SUMMARY

The RF dielectric barrier discharge plasma, operated at atmospheric pressure, was utilized for the plasma treatment of nano-structured carbon powder. The large-size coagulated flakes consisted of nano-size particles were broken into smaller-size particles by partial etching of the carbon between the fine particles using the plasma of Ar together with a small amount of oxygen. This small plasma device at atmospheric pressure can continuously treat powdery material.

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