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Development and diagnostics of novel materials processing using supercritical fluid plasma generated by space- and time-restricted discharge

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Plasma generated in supercritical fluid (SCF) is anticipated to yield a unique reactive field due to a combination of the high reactivity of plasma and the superior transport properties and density fluctuation of SCF. To effectively use the unique characteristics of SCF, it is important to prevent an increase in gas temperature, which degrades the unique characteristics of SCF. The space and time restrictions of the plasma have been the typical methods for keeping the gas temperature of the plasma generated in a high-pressure environment low. In our previous study, it was found that a reduction in plasma size contributes markedly to the appearance of the novel phenomenon of discharge generated in SCF. In this work, using pulsed DC voltage, we generated time-restricted discharge plasmas in supercritical CO_2 and discuss the effect of the time restriction of the plasma generation by pulse technology on the SCF plasma and SCF plasma processing. Moreover, using nanosecond-order pulsed DC voltage, we successfully fabricated carbon nanomaterials, such as carbon nanotubes (CNTs), from CO_2, without the electrode being seriously damaged by the discharge plasma in a supercritical CO_2 environment.
Key words: supercritical fluids, microplasma, pulsed discharge, carbon nanomaterials, CO_2

1. INTRODUCTION

The applications of supercritical fluid (SCF) have expanded dramatically in various fields because SCF is considered to be a promising alternative to flammable and toxic conventional organic media, not only in environmental, reaction chemistry and semiconductor fields, but also in the fields of materials synthesis and processing [1-3].

In addition, recently, the plasma generated in SCF (SCF plasma) has attracted much interest due to its promising characteristics, which results from a combination of the high reactivity of plasma and the excellent transport properties of SCF, such as its liquid-like high density, gas-like low viscosity, zero surface tension and high diffusivity [4].

From a microscopic point of view, SCF consists of clusters of various sizes and, especially, near the critical point, exhibits a large density fluctuation [5]. Therefore, SCF plasma is anticipated to create a novel plasma reaction field that contains radical/ion clusters, in addition to electrons, ions, atoms and molecules.

After our pioneering work on SCF discharge plasma [6], some groups have started reporting their interesting studies on this topic in recent years [7-12].

In general, the environmental temperature of plasma generated in a high-pressure environment is liable to rise intensively, because of the high collision frequency between electrons and molecules. However, the above-mentioned transport properties and molecular clustering state of SCF near its critical point can be easily changed by slight changes in the temperature and pressure. In other words, even a slight increase in temperature induced by the plasma generation might result in a drastic change in the unique characteristics of SCF.

To keep the environmental temperature inside the plasma low, it is known that reducing the size of plasma is effective. Generally, following a scaling law, such as Paschen's law, miniaturization of DC discharge plasma toward Paschen's minimum, which is the most efficient condition for plasma generation, facilitates low-temperature plasma (e.g., glow discharge plasma) generation under a high-pressure condition. Moreover, as the plasma size decreases, the ratio of the surface area to the volume becomes larger. Therefore, heat that accompanies the generation of discharge may easily escape from the discharge space and it is highly

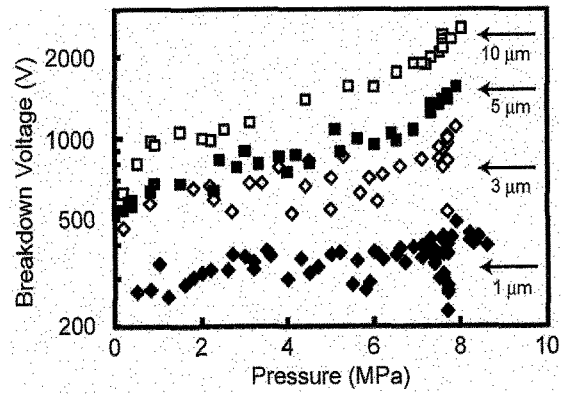
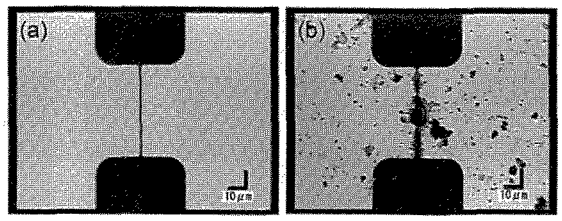


Fig.1. Breakdown voltages of DC discharge in high-pressure CO_2 with electrodes of 1 (closed diamond), 3 (opened diamond), 5 (closed square), and 10 (opened square) μm gap distances .



Figs.2. Photographs of Pt CFEs (a) before and (b) after continuous DC discharge generated in supercritical H_2O.

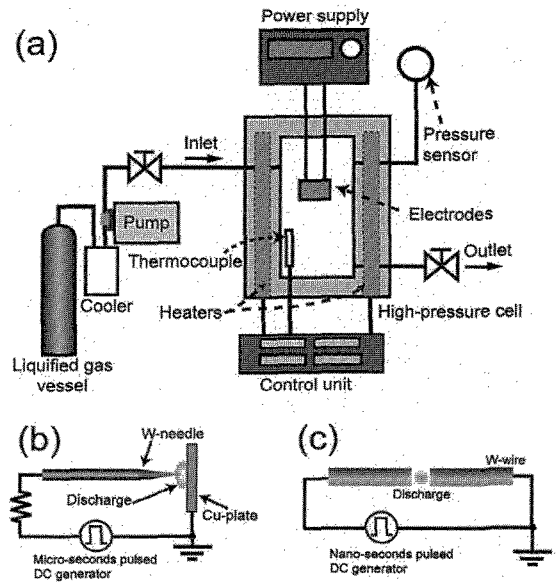
anticipated that clusters will sustain their structures even though they are in the discharge space.

In our previous study, we succeeded in generating micrometer-scale DC discharge plasma in SCF, and found that in the breakdown stage, the reduction in discharge plasma size contributed to the appearance of the novel phenomena of DC discharge generated in supercritical CO_2, H_2O and Xe environments [6-8].

Fig.1 shows the breakdown voltage of DC discharge measured in high-pressure CO_2 up to supercritical conditions (the critical point: 7.38 MPa, 304.2 K) using coplanar film electrodes (CFEs) with a 1-10 μm gap. According to the results, the breakdown voltages of 1- and 3-μm-gap electrodes show a drastic decrease near the critical points simultaneously with the increase in density fluctuation. This phenomenon is anticipated to be caused by the void, where the electron can be accelerated, created by the large density fluctuation of SCF. It was also found that this unique behavior depends on the gap width. When the discharge gap is larger than 5 μm, the temperature of the discharge space may locally become much higher than the critical temperature and the clustering structures are destroyed. Therefore, no drastic decrease in breakdown voltages might be observed with the CFEs with larger gaps. The detailed discussion about this unique behavior of the breakdown voltage and its dependence on the discharge gap is presented in Ref.8.

As mentioned above, it is anticipated that the reduction in plasma size is effective for the creation of the novel plasma state, which coexists with the unique characteristics of SCF. However, in the case of continuous DC discharge, the gas temperature in the plasma tends to increase intensively during the plasma generation. Figs.2 show photographs of Pt CFE (a) before and (b) after continuous DC discharge is generated in supercritical H_2O in a period of several seconds. From the photograph as shown in Fig.2(b), the edges of the electrodes facing the discharge seem to be melted and rounded. Therefore, the gas temperature of the plasma is expected to be above the melting point of Pt (about 2040 K). This damage of the electrode might be serious for the materials processing and the diagnostics, which require a stable generation of plasma.

In this study, to reduce the damage of the electrodes caused by discharge, we applied pulsed DC voltage to the generation of discharge plasma in SCF. It is known that reducing the plasma generation time is effective for keeping the gas temperature low and the creation of non-equilibrium reactive fields. Therefore, we employed microsecond- and nanosecond-order pulsed DC voltage to generate SCF plasma and discuss the effect of temporal restriction on SCF plasma. Moreover, we also



Figs.3. Schematic diagrams of (a) typical apparatus for the discharge plasma generation in a high-pressure environment, (b) electrodes for microsecond-order pulsed DC discharge plasma, and (c) electrodes for nanosecond-order pulsed DC discharge plasma.

fabricated the carbon nanomaterials, such as carbon nanotubes (CNTs), from CO_2 using the SCF plasma.

2. EXPERIMENTAL

The experimental setup for generating discharge plasma in a high-pressure environment is shown in Fig.3(a). First, liquefied CO_2 condensed in a condenser is pumped up to the high-pressure cell. Then, pressure and temperature in the cell were monitored using a sensor and a thermocouple, respectively, and were controlled using heaters or temperature-controlled water to create a high-pressure environment including supercritical conditions. Electrodes are fixed in the cell. The emission spectra of plasmas can be measured through the sapphire window with a charged-coupled device (CCD) camera (Spec-10: 2KB/LN, Princeton Instruments Inc., NJ, USA) and a 500 mm spectrometer (SpectraPro-500i SP-556, Acton Research Corp., MA, USA). The spectra were recorded with a computer (PC).

Fig.3(b) shows a schematic diagram of the electrodes for microsecond-order pulsed DC discharge plasma. The electrodes consist of a W needle and a Cu plate. The distance between electrodes is approximately 100 μm. The pulse width is about 400 μs. The voltage for the generation of discharge was applied through a resistor (15 MΩ). Fig.3(c) shows a schematic diagram of the electrodes for nanosecond-order pulsed DC discharge plasma. The pulse width is about 50 ns. The electrodes consisted of two W wires, whose ends were mechanically polished to be flat. The distance between electrodes is less than 50 μm.

3. RESULTS AND DISCUSSION

3.1 Microsecond-order discharge plasma

The repetitive application of DC voltage pulses causes the cooling period to lie between plasma generation periods, which is important for materials synthesis using

plasmas, because the materials are formed in the cooling process.

In this experiment, we generated the discharge plasma in supercritical CO_2 applying repetitive 400 μs pulsed DC voltage (pulse frequency: 5 Hz) and the relatively long duration (more than 10 min) plasma processing and diagnostics were carried out. To date, we have successfully synthesized carbon nanomaterials (e.g., carbon nanotubes (CNTs)) from CO_2 using this microsecond-order pulsed DC discharge generated in supercritical CO_2. The details of the condition and synthesized materials were described elsewhere [9].

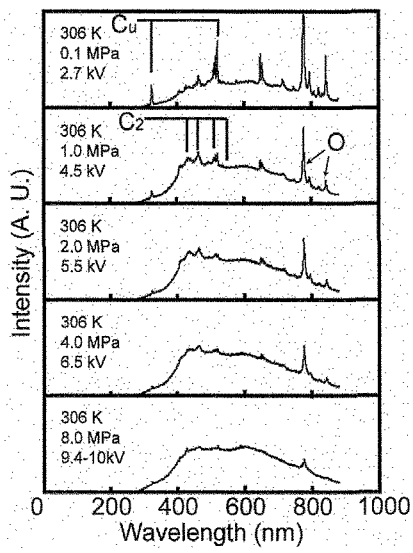
Figs.4 shows the typical emission spectra of the microsecond-order pulsed DC discharge generated in a high-pressure CO_2 environment up to supercritical condition. It was found that as the pressure increases, the shape of the spectra becomes a continuum one and the peaks of C_2 and O are remarkable in intensity. It is considered that CO_2 is dissociated by the plasma and the carbon precursor originating from CO_2 formed carbon nanomaterials.

3.3 Nanosecond-order discharge plasma

Although applying the microsecond-order pulsed DC voltage could extend the plasma processing time, the damage of the electrode is still remarkable. In addition, from the OES measurement, the emission peaks of Cu, the material of the electrode, were observed in Figs.4 and the gas temperature estimated from the N_2 rotational temperature was 800 K in supercritical N_2 [13].

Therefore, it is supposed that the increase in temperature caused by the microsecond-order pulsed DC discharge plasma might degrade the unique characteristics of SCF, such as density fluctuation, and the further shortening of the plasma duration is preferred for the effective use of the unique characteristics of SCF.

Then, we applied two methods for the reduction of plasma duration up to the nanosecond scale. One method is the use of dielectric barrier discharge (DBD). DBD is employed in plasma display panels (PDPs), and can be



Figs.4. Emission spectra taken from microsecond-order pulsed DC discharge plasmas in high-pressure CO_2 environment up to the supercritical condition.

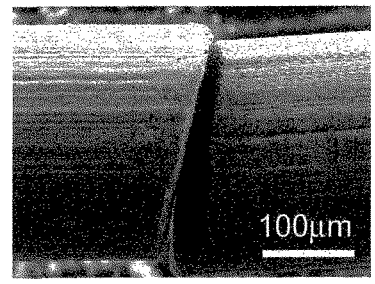


Fig.5. SEM image of electrodes after repetitive 50-ns pulsed DC discharge (100 Hz) generated in supercritical CO_2 for 1 hour.

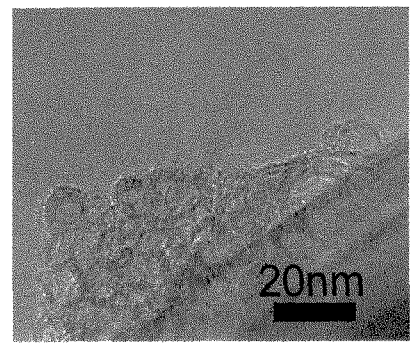


Fig.6. TEM image of carbon nanomaterials synthesized from CO_2 using pulsed discharge generated in $scCO_2$.

generated between two electrodes, at least one of which is covered with a dielectric barrier, when an AC voltage is applied to the electrodes. The dielectric charged by the electrons transferred in a discharge interrupts the discharge and the duration of one discharge is spontaneously restricted to less than 100 ns. In our previous study, it was found that the DBD can be used to create low-temperature plasma reactive fields in SCF [10].

The other method is the use of the nanosecond-order pulse power technique. In this study, we generated nanosecond-order pulsed DC discharge plasma for materials synthesis. In a previous study, Akiyama's group reported that using nanosecond-order pulsed power (pulse width: < 1 μs), non-equilibrium plasma can be generated in a liquid [14]. Recently, they generated the streamer discharge in SCF applying nanosecond-order pulsed DC voltage to induce chemical reactions.

Fig.5 shows a scanning electron microscopy (SEM) image of the electrodes after repetitive 50-ns pulsed DC discharge (repetition frequency: 100 Hz) generated in supercritical CO_2 for 1 hour. The serious damage of the electrodes was hardly observed. It is supposed that shortening the discharge duration prevents the gas temperature from rising and the nanosecond-order pulsed discharge plasma may not degrade the unique characteristics of SCF.

Fig.6 shows an example of a transmission electron microscopy (TEM) image of carbon nanomaterials synthesized using pulsed discharge generated in supercritical CO_2. The synthesized CNTs seem to be short and distorted compared with those synthesized using microsecond-order pulsed DC discharge plasma. It is supposed that further reducing the plasma duration up

to the nanosecond scale might increase the effect of the fluctuation/molecular clustering on the formation of carbon nanomaterials.

4. CONCLUSION

In this study, we generated pulsed DC discharge plasmas in SCF and discussed the effect of time restriction on SCF plasma and SCF plasma processing. It was found that shortening the plasma duration could reduce the damage of the electrodes caused by discharge plasma in SCF. Moreover, it is anticipated that, in addition to limiting the plasma size, limiting the plasma duration might be effective for the creation of a novel plasma state, which coexists with the unique characteristics of SCF.

This space- and time-restricted SCF plasma might yield space- and time-localized materials processings, such as micrometer-scale and highly time controlled deposition and surface treatment, using the SCF plasma. Moreover, time- and space-arraying the plasma reaction fields using multiple electrodes and increasing the pulse frequency as in PDPs might facilitate the development of practical massive materials processings on an industrial scale.

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References

[1] J. D. Holmes, D. M. Lyons and K. J. Ziegler, Chem. Eur. J., **9**, 2144 (2003).
[2] M. Poliakoff and P. Anastas, Nature (London), **413**, 257 (2001).
[3] A. I. Cooper, Adv. Mater., **13**, 1111 (2001).
[4] A. Eckert, B. L. Knutson and P. G. Debenedetti, Nature (London), **383**, 313 (1996).
[5] K. Nishikawa, I. Tanaka and Y. Amemiya, J. Phys. Chem., **100**, 418 (1996).
[6] T. Ito and K. Terashima, Appl. Phys. Lett., **80**, 2854 (2002).
[7] T. Ito, H. Fujiwara and K. Terashima, J. Appl. Phys., **94**, 5411 (2003).
[8] M. Sawada, T. Tomai, T. Ito, H. Fujiwara and K. Terashima, J. Appl. Phys., **100**, 123305 (2006).
[9] T. Ito, K. Katahira, Y. Shimizu, T. Sasaki, N. Koshizaki and K. Terashima, J. Mater. Chem., **14**, 1513 (2004).
[10] T. Tomai, K. Katahira, H. Kubo, Y. Shimizu, T. Sasaki, N. Koshizaki and K. Terashima, J. Supercritical Fluids, **41**, 404 (2007).
[11] E. Lock, A. Saveliev and L. Kennedy, IEEE Trans. Plasma Sci., **33**, 850 (2005)
[12] C. H. Zhang, T. Kiyan, T. Namihira, A. Uemura, S. Katsuki, H. Akiyama, T. Fang, M. Sasaki and M. Goto, Proc. Industry Applications Society, 40th Annual General Meeting, 2005, pp. 1845-1848.
[13]T. Tomai, M. Sawada and K. Terashima, 17th Proc. International Symposium of Plasma Chemistry, 2005, No. 676.
[14] H. Akiyama, IEEE Trans. Dielectr. Electr. Insul., **7**, 646 (2000).

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