Observation of Particulate Matter Combustion in a Pulsed Discharge Duration*

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A system is developed for the observation of the combustion of diesel particulate matter (PM) in a pulsed discharge. This system includes a dielectric barrier discharge reactor, a pulse power supply, a monochromator connected to a high dynamic range streak camera, and a measurement system of discharge voltage and current waveforms. Luminescence from the discharge gap fed with PM and O_2 can be observed when a pulsed voltage is applied. It has been found that the luminescence from the discharge gap with PM and O_2 is due to the presence of CO_2 or CO, where CO_2 and CO are the products of PM combustion with O_2.

Keywords: diesel particulate matter, combustion, DBD, pulsed discharge, luminescence, spectrum.

1. Introduction

Plasma discharges are under development for the removal of particulate matter (PM) emitted from a diesel engine [1]. PM is mainly composed of soot (graphitic-like carbon) and organic-soluble fraction (SOF). The authors have demonstrated that PM can be oxidized to carbon oxides (CO and CO_2) by active oxygen species (such as O atoms) [2] and UV radiation generated by plasma discharges in oxygen atmosphere. Related with the mechanism of PM removal in plasma discharges, the mechanism of carbon materials of the same basic structural element graphene is helpful. Grujicic *et al*. calculated the interactions between selected semiconducting and metallic single-walled carbon nanotubes (as well between single and double graphene sheets) and found that UV-light excitation of the O_2-molecules from their ground spin-triplet state to a higher-energy spin singlet state can give rise to a significant reduction in the activation energy for O_2-molecule chemisorption and, hence, increases significantly the rate of nanotube oxidation [3]. Liu *et al*. (2006) have proposed an unzipping mechanism to explain the observed so-called fault lines and cracks on graphite oxide (GO) [4]. The strain generated by the cooperative alignment of epoxy groups can initiate cracks on GO. The continuation of unzipping process can be achieved by binding of a new epoxy ground during oxidation or hopping of an existing epoxy group and subsequent locking. The O atoms those can be produced by plasma discharges play an important role in the formation of epoxy groups on GO. Oxidation and UV radiation have been used to manipulate carbon materials as in the case of carbon nanotube cutting [3,5]. We also found that sp^2 bonding carbon in PM is converted to sp^3 bonding carbon and -C-OH, -C=O and -COOH compounds are generated by plasma discharges; this fact implied that PM is truly oxidized by plasma discharges [6].

As the carbon oxidation is a process with luminescence, the dark field optical microscope images were used to examine GO [7]. However, there is no the direct evidence to show that PM is burned to CO and CO_2 in plasma discharges. In this study, a system is developed for the observation of PM combustion in a pulsed discharge.

2. Experimental

Figure 1 shows the experimental system including a single channel discharge (SCD) reactor, a pulse power supply (DP-30K10, Peec), a discharge voltage/current measuring system, and a monochromator (C-5094, Hamamatsu) connected to a high dynamic range streak camera (C7700, Hamamatsu). As shown in Fig. 2, the SCD reactor consisted of two alumina plates (99.5% purity, 50×50×1.0 mm^3), two alumina tubes (Φ10OD×Φ6ID×29 mm^3), and two stainless steel rod electrodes (Φ6×85 mm^2). The gap distance between two alumina plates was fixed at 6.8 mm or 2 mm. The SCD reactor was installed in an acrylic resin box of two quartz windows. Oxygen (99.9999% purity) or CO_2 (99.9999% purity) was fed to the discharge gap at a flow rate of 100 ml/min. The waveforms of discharge voltage and anode and cathode currents were measured using a voltage probe (V-P, P6015A, bandwidth DC~75 MHz, Tektronix) and two current transformers (CT1 and CT2, A6312, bandwidth DC~100 MHz, Tektronix) with two current probe amplifiers (AM503B, Tektronix), respectively. The signals from the voltage probe and two current probe amplifiers were digitized and recorded using a digital phosphor oscilloscope (TDS 7104, bandwidth 1 GHz, Tektronix). The pulse power supply was used to supply pre-trigger signals (11 ms before each voltage pulse) and positive pulsed voltage to the SCD reactor at a single

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pulse mode. The luminescence from the discharge gap was measured optically using the monochromator. The entrance slit width of the monochromator was 500 μm for spectrum measurements at various discharge times grating at 100 gr/mm and at a central wavelength of 500 nm and, 1000 μm for image recording of the luminescence at various discharge times with spectral separation (at a wavelength setting of 0). The spectra and images were recorded using the streak camera with the streak slit (2.0 mm) located in the image plane of the monochromator exit. The streak camera was controlled with a computer (PC), a signal generator (DG533, Stanford Research System), and the pre-trigger signal from the pulse power supply. The recording time of the streak camera was monitored using the digital phosphor oscilloscope. As shown in Fig. 2, 1.2 milligrams of PM were put on the surface of one alumina plate. The PM was collected from the exhaust gases of a 4-cycle diesel engine. The PM thermal combustion in oxygen atmosphere was carried out using a thermogravimetric-differential thermal analyzer (TG-DTA, Thermal Pulse-8120, Rigaku) equipped with a mass spectrometry (MS, M-200QA, Anelva).

All discharge experiments were conducted at atmospheric pressure and room temperature (298 K) without heating except plasma discharge heating.

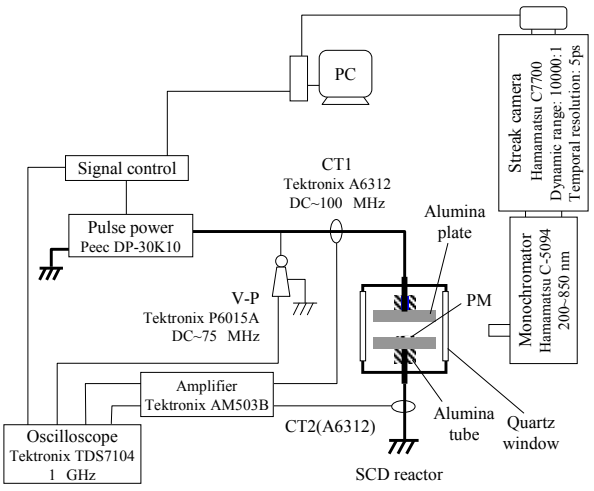

Fig.1 Experimental set-up.

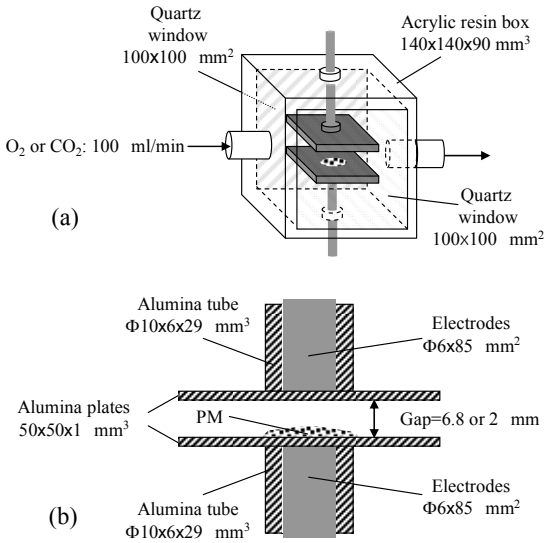

Fig.2 Configuration and structure of the SCD reactor (a) and basic structure of the discharge gap with PM (b).

The energy injection P_d in joules per pulse and power injection in kW were calculated using Eqs. (1) and (2), respectively, over one pulse discharge duration.

$$P_d = \sum_i \left(\frac{V_{i+1}+V_i}{2}\right)\left(\frac{I_{i+1}+I_i}{2}\right)(t_{i+1}-t_i) \quad (1)$$

$$P = \frac{1}{1000}\sum_i \left(\frac{V_{i+1}+V_i}{2}\right)\left(\frac{I_{i+1}+I_i}{2}\right) \quad (2)$$

Where, V_{i+1} and V_i, are discharge voltage in volts at discharge times t_{i+1} and t_i in seconds, respectively. I_{i+1} and I_i are cathode currents in amperes at discharge times t_{i+1} and t_i, respectively. The values of discharge voltage and currents were from the waveforms of discharge voltage and cathode current.

3. Results and discussion

3.1 PM thermal combustion

Before experiments of PM combustion in a pulsed discharge, PM thermal combustion was measured using the TG-DTA and MS. The result is shown in Fig. 3. The heat flow due to the PM combustion became to increase at 570 ^{o}C, indicated that PM combustion happened at the temperature above 570 ^{o}C. Ninety one percent of PM burned at 672 ^{o}C. The main products of PM combustion were found to be CO and CO_2.

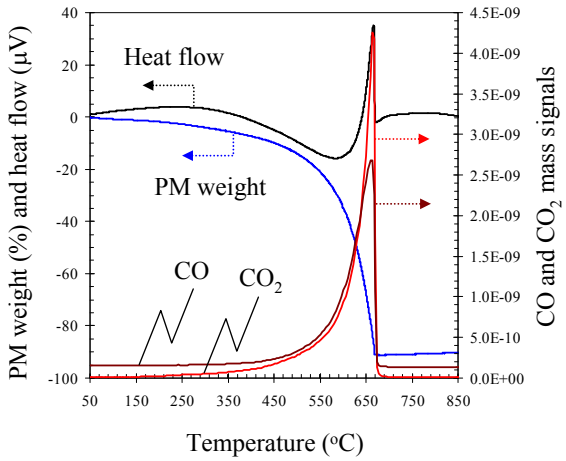

Fig. 3 PM thermal combustion in oxygen-containing atmosphere. Experimental condition: O_2 concentration: 10% (helium balance), scanning temperature rate: 10 °C/min.

3.2 Energy injection and luminescence

Typical energy injection at various times is illustrated in Fig. 4. The energy injection starts at time 41.6 μs and peaks at time 43 μs with a level of 13.9 kW. The energy injection becomes zero after time 60 μs.

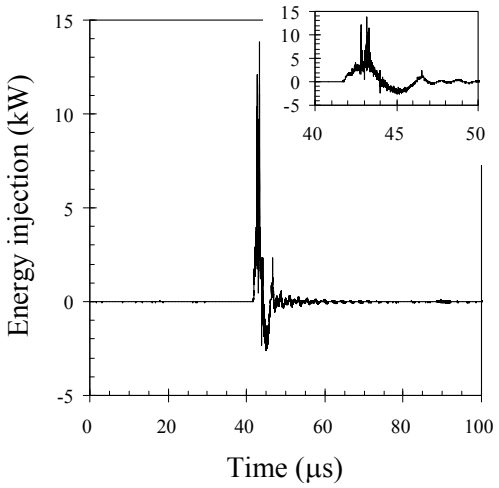

Fig.4 Energy injection to the discharge gap (6.8 mm, fed with O_2) with PM at various discharge times. The small figure is the energy injection between a time range of 40-50 μs.

Figure 5 shows images of the luminescence from the discharge gap with or without PM. The luminescence from the discharge gap with PM has been observed. This luminescence is obviously due to the presence of PM in the discharge gap. However, no remarkable luminescence from the discharge gap without PM could be observed under the condition that the discharge exactly occurred.

3.3 Spectrum of PM combustion in a pulsed discharge

Related with the luminescence from PM particles, laser-induced incandescence (LII) has been developed for measurements of soot particles [8]. A pulse laser beam is used to vaporize PM by heating PM to an elevated temperature (several 1000s K) at which the magnitude of the incandescence is used to estimate the soot diameter and volume fraction. The measurement using LII technique is based on the microphysical description. As a fact that PM can be oxidized by oxygen at a temperature higher than about 570 °C, the soot particles undergo oxidation after being heated by laser radiation. Michelsen evaluated the probability of soot oxidation based on molecular oxygen. They found the oxidation probability of soot is less than 0.1 even at an elevated temperature of 5000 K due to laser radiation in oxygen-containing atmosphere [8]. However, a large amount of O atoms can be produced by plasma discharges. As O atoms are more reactive than O_2 molecules, the oxidation of PM in plasma discharges should be accounted. We then measured the spectrum of the luminescence from the discharge gap with PM to find whether PM combustion happens in a pulsed discharge.

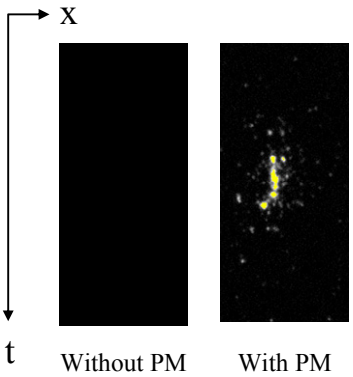

Fig.5 Images taken from the discharge gaps (6.8 mm, fed with O_2) without PM and with PM. The energy injections were 3.69 mJ (without PM) and 3.76 mJ (with PM). x is the gap position in the horizontal axis as shown in Fig. 2(b). t is the time axis.

As shown in Fig. 6, no remarkable lines could be found from the discharge gap without PM. Many lines can been observed from the discharge gap with PM; those lines locate in wavelength ranges of 300-390 nm, 400-480 nm, 480-520 nm, 520-580 nm, and 700-720 nm. In order to identify the spectra, the spectra from a 2-mm discharge gap fed with O_2 or CO_2 were measured. The normalized intensities of the spectra from the 6.8-mm discharge gap with PM and O_2 and from the 2-mm discharge gap fed with CO_2 only are shown in Fig. 7. It must be noted that no detectable luminescence from the 2-mm discharge gap fed with O_2 only was found. Most lines on the spectrum with PM and O_2 locate at the same positions as those on the spectrum with CO_2. As CO_2 can be converted to CO by plasma discharges, CO is then

present within the discharges gap. Therefore, the luminescence from the discharge gap with CO_2 is due to the presence of CO and CO_2 that are excited by energized electrons in the pulsed discharge space. The difference in CO and CO_2 concentrations causes possibly the difference in intensity between each spectral line as shown Fig. 7. It should be noted that the combustion of PM is obviously not due to the thermal combustion as the maximum gas temperature due to plasma discharge heating is less than 170 ^oC, far lower than that (570 ^oC) required for PM thermal combustion. As the products of PM combustion are CO_2 and CO, those findings suggested that PM combustion occurred by reactive oxygen species, such as reactive O atoms, singlet O_2, and UV light [3] those generated by the pulsed discharge.

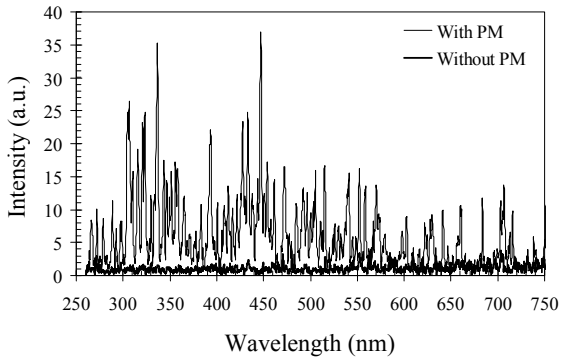

Fig.6 Spectra of the luminescence from the discharge gap (6.8 mm, fed with O_2) with PM and without PM. The energy injections were 3.57 mJ (without PM) and 3.3 mJ (with PM).

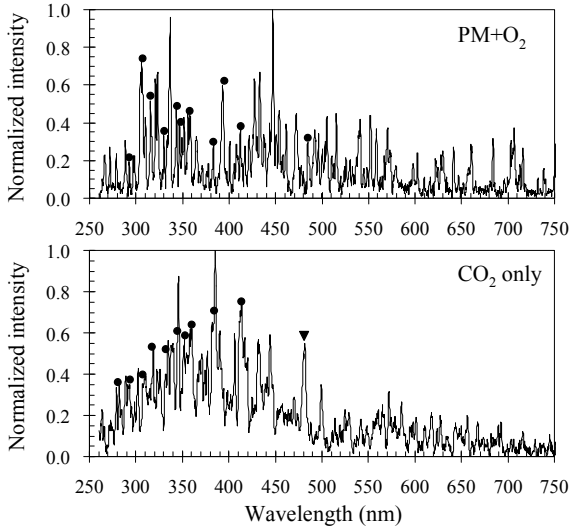

Fig. 7 Spectra of the luminescence from the discharge gap (6.8 mm, fed with O_2) with PM ($PM+O_2$) and from the discharge gap (2 mm, fed with CO_2) without PM (CO_2 only). The energy injections were 3.3 mJ ($PM+O_2$) and 3.5 mJ (CO_2 only). ● and ▼ denote CO and CO_2 lines, respectively.

4. Conclusion

A system used for observation of PM combustion in a pulsed discharge using a DBD reactor fed with O_2 has been established. The main conclusion is summarized as follows:

1) PM thermal combustion in 10% oxygen atmosphere occurs at a temperature higher than 570 ^oC.
2) Luminescence from the discharge gasp fed with PM and oxygen can be observed in a pulsed discharge.
3) The luminescence is due to the presence of CO_2 and CO that are excited by energized electrons in the pulsed discharge space, where CO_2 and CO are the products of PM combustion with O_2.

5. References

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