

APPLICATION OF PSP IN LOW PRESSURE REGIME

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ABSTRACT

The PSP technique has the capability to be applied to high Knudsen number flows, such as low density gas flows, micro-flows, and so on. In this study, fundamental properties of PSPs such as sensitivity to pressure are examined especially in the range of pressure below 150 Pa (about 1 Torr), to select the most suitable PSP for the low pressure range. One of the PSP is Bath-Ru adsorbed directly on anodized aluminum, and the other PSPs are composed of porphyrin complexes bound by glassy polymer poly(TMSP). As an application of PSP to low density gas flows, we measure a pressure distribution on a surface of an aluminum plate interacting with a low density supersonic free jet. The clear two-dimensional pressure distribution was obtained by using PtTFPP/poly(TMSP), showing the feasibility of quantitative pressure measurement using the PSP.

INTRODUCTION

In the recent development of high-technology, rarefied gas flows become more important, related to the aerospace science, formation of thin films for semiconductors and so on. Rarefied gas flows with high Knudsen number cannot be analyzed by methods used for analyses of continuum flows, because the intermolecular collision rate is extremely small and effects caused by molecular motions are significant. Therefore, diagnostic tools in the molecular level are required for analyses of rarefied gas flows. Moreover, flows in microsystems with small dimension has also high Knudsen number and they must be treated as rarefied gas flows. Especially, there may be no detailed information yet about the behavior of molecules in the vicinity of the solid surface and the energy exchange between the molecules and the surface, motivating development of new measurement techniques in the molecular level.

Recently, many studies related to pressure measurements on solid surfaces using PSP have been reported¹⁾⁻⁵⁾. In the studies, pressure on a surface is deduced from the calibration curve, which is obtained in the range of pressure larger than about 1 Torr (133.3 Pa). Since luminescence intensity decreases as an increase in partial pressure of oxygen gas and does not change significantly in low pressure range, PSP techniques have been considered inadequate to be applied to rarefied gas

flows. It prevents from using the PSP in the low pressure range. However, PSP techniques are based on energy transfer in molecular level such as quenching of organic luminophores, and they have potential for applications in high Knudsen number regime, where molecules play an important role.

In this study, we select several types of PSP, and examine their fundamental properties such as pressure sensitivity, temperature dependence of luminescence intensity and response of luminescence intensity on pressure change in the range of pressure below 150 Pa (about 1 Torr). Finally, the pressure distribution on a solid surface interacting with a low-density supersonic free jet is measured by the PSP, and the feasibility of PSP for quantitative measurement is examined.

LUMINESCENCE PROPERTIES OF PSP

In the PSP technique, pressure can be measured by oxygen quenching of luminescence^{2),3)} emitted from the luminescent molecules irradiated by a UV light. High luminescence intensity corresponds to the low pressure region and low intensity to the high pressure region. Pressure on the solid surface can be deduced from the relationship between pressure and the luminescence intensity (Stern-Volmer plot).

Stern-Volmer equation

Luminescence quantum yield Φ of PSP is given by³⁾

$$\Phi = \frac{I}{I_a} = \frac{k_L}{k_L + k_D + K_Q[O_2]} = K_L\tau, \quad (1)$$

where I is the luminescence intensity and I_a is the absorption intensity. k_L , k_D , and K_Q are the rate constants for luminescence, radiationless deactivation and oxygen quenching, respectively. $[O_2]$ is the concentration of oxygen molecules, and τ the lifetime of an excited luminescent molecule.

From Eq. (1), the ratio of the luminescence intensity I to that in the absence of oxygen molecules I_0 is given by

$$\begin{aligned} \frac{I_0}{I} &= \frac{k_L + k_D + K_Q[O_2]}{k_L + k_D} = 1 + \frac{K_Q[O_2]}{k_L + k_D} \\ &= 1 + K_Q\tau_0[O_2], \quad (2) \end{aligned}$$

where τ_0 is the lifetime of an excited molecule in the absence of oxygen molecules. The concentration $[O_2]$, the partial pressure of oxygen gas P_{O_2} , and the total

pressure P follow the relation $[O_2] \propto P_{O_2} \propto P$, according to Henry's law. Because K_Q and τ_0 depend on the temperature T , Eq. (2) can be put in a form

$$I_0/I = 1 + K(T)P, \quad (3)$$

where K is a constant depending on T .

In a practical application of PSP, it is usually difficult to measure I_0 to calibrate the PSP. If the luminescence intensity of the PSP I_{ref} is obtained at the known reference pressure P_{ref} , Eq. (3) is modified as follows,

$$\frac{I_{ref}}{I} = A_0(T) + A_1(T) \frac{P}{P_{ref}}. \quad (4)$$

The luminescence intensity I of the ideal PSP depends inversely on P as mentioned in Eq. (4), but the actual PSPs show nonlinearity of I on P . Therefore, the following equation considering the nonlinearity should be employed:

$$\frac{I_{ref}}{I} = \sum_{n=0}^N A_n(T) \left(\frac{P}{P_{ref}} \right)^n. \quad (5)$$

The A_n in Eqs. (4) and (5), called as Stern-Volmer coefficients, are the coefficients determined by the calibration tests. In practice, a second-order polynomial ($N = 2$) is commonly used³.

Temperature Dependence of Luminescence Intensity

Temperature dependence of the coefficients A_n in Eq. (5) is caused by that of k_L , k_D and k_Q . It is the last two rate constants that exert an influence on the luminescence intensity. The rate constant for radiationless deactivation k_D can be expressed by the sum of a temperature-independent term k_0 and a temperature-dependent term k_1 (i.e., $k_D = k_0 + k_1$). The rate constant k_1 is given by the Arrhenius equation³,

$$k_1 = C \exp(-E/R_0T), \quad (6)$$

where C is a constant, E the Arrhenius activation energy, and R_0 the universal gas constant. Eq. (6) mentions that k_1 increases as an increase in temperature T , so that k_D also increases and, as evidenced by Eq. (1), the luminescence intensity I decreases as T increases. When using polymer as a binder, the rate constant for oxygen quenching k_Q is usually dominated by the diffusion coefficient of oxygen molecules in the polymer layer, which depends strongly on T . The k_Q is given by the Smoluchowski relation³,

$$k_Q = 4\pi N p D_Q, \quad (7)$$

where N is the number of molecules per millimole and p is a factor that depends on the quenching mechanism. D_Q is the diffusion coefficient of oxygen molecules and its dependence on T is also given by the Arrhenius equation³,

$$D_Q \propto \exp(-E_Q/R_0T), \quad (8)$$

where E_Q is the activation energy related to the diffusion of oxygen molecules in the polymer. D_Q increases as an increase in temperature T , leading to an increase of k_Q as shown in Eq. (7). Therefore, it is clear from Eq. (1) that the luminescence intensity I decreases as an increase in temperature T . The diffusion coefficient D_Q depends also on a kind of polymer, and the larger the D_Q is, the higher the pressure sensitivity of PSP is and the more useful the binder with the large D_Q becomes especially for applications of PSP to the rarefied gas flows.

LIST OF PSP

In this study, two types of PSPs are examined in low-pressure range below 150 Pa, and the most suitable PSP in low pressure conditions is proposed by clarifying the feasibility and problems of the PSPs. In this paper, we call the PSPs as [luminophore]/[binder] (e.g. PtTFPP/poly(TMSP) and Bath-Ru/AA).

One type of PSP is composed of Bath-Ru [Ruthenium II tris (4,7-diphenyl-1,10-phenanthroline) chloride] adsorbed on a porous surface of anodized aluminum (AA). Bath-Ru/AA utilizes no polymer binder to fix the luminophore Bath-Ru onto the solid surface, but Bath-Ru molecules are bound directly on the anodized aluminum surface. Because the luminophore is exposed to the atmosphere, Bath-Ru/AA has fast response time and high sensitivity to oxygen pressure even in a cryogenic conditions^{4,5}. However, it can be applied only to aluminum or aluminum alloys.

The other type of PSP utilizes poly(TMSP), a glassy polymer with extremely high oxygen permeability, as a binder. We applied PtTFPP, PdOEP, and PdTFPP as luminophores bound by poly(TMSP). The PSPs have high advantages such as high sensitivity, fast response time, and capability of measurement in cryogenic conditions. Moreover, they can be applied to any materials, unlike Bath-Ru/AA.

The properties of the PSPs mentioned above in low oxygen pressure are compared with that of PtOEP/GP197, one of the pioneer PSPs developed at the University of Washington¹.

EXPERIMENTAL APPARATUS

Figure 1 shows the experimental apparatus composed for this study. The PSPs are painted on aluminum plates (50mm×25mm×1mm) and then the plates are set inside a vacuum chamber evacuated by a rotary pump (ULVAC D-950) or a turbo molecular pump (ULVAC UTM-300). Pure oxygen gas is supplied into the chamber in which pressure is kept at 1.0×10^{-2} –150 Pa. A sonic nozzle can be attached at the supply port of oxygen gas to carry out the experiments for a supersonic free jet impinging on the solid surface using the same vacuum chamber. The pressure is monitored by a capacitance manometer

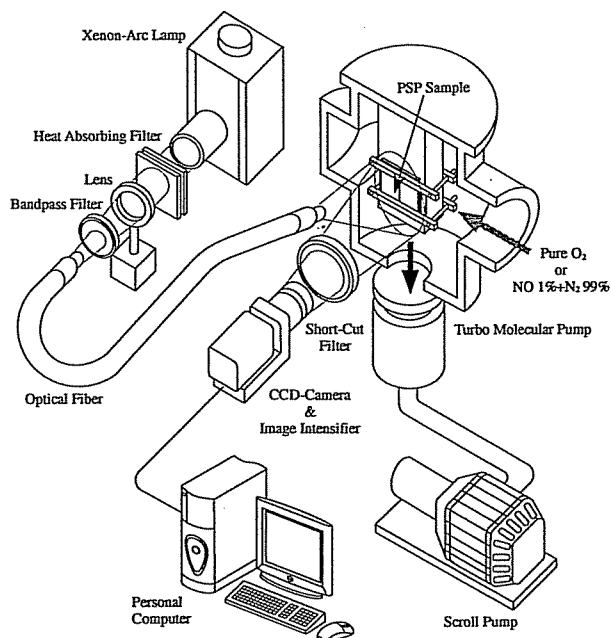


Figure 1 Experimental Apparatus

(ULVAC CCMT-10A) and an ionization vacuum gauge (ULVAC GI-1000). Using a Peltier thermo-controller and a thermocouple, the temperature of the PSP sample is kept at 300 K (except for PtOEP/GP197, which is kept at 293 K). A xenon-arc lamp (Ushio UXL-500SX) with a band-pass filter is used as an excitation light source, and the light is transmitted via an optical fiber to illuminate the sample in the vacuum chamber. The wavelength ranges of the band-pass filters are 380 ± 20 nm for PtOEP, 450 ± 10 nm for Bath-Ru, and 400 ± 10 nm for PtTFPP, PdOEP, and PdTFPP, which cover the absorption spectrum of each luminophore. The luminescence is filtered by a long-pass filter (600 nm) to eliminate the light from the xenon lamp, and is detected by a CCD camera (Hamamatsu, C7300-10) with an image intensifier (Hamamatsu, C6653). The image of the luminescence is processed by a personal computer and the luminescence intensity is averaged over 200×200 pixels of the CCD camera.

RESULTS AND DISCUSSIONS

Stern-Volmer plots of the PSPs

Figure 2 shows the Stern-Volmer plots of PtOEP/GP197, Bath-Ru/AA, PtTFPP/poly(TMSP) at low pressure below 150 Pa. The horizontal axis is the pressure on the sample surface, and the vertical axis is I_{ref}/I mentioned in Eq. (5). The surface temperature of each sample is kept at 300 K (but PtOEP/GP197 is kept at 293K). The pressure ranges are 1.0×10^{-2} –151 Pa for PtOEP/GP197, 1.0×10^{-2} –152.5 Pa for Bath-Ru/AA, 1.0×10^{-2} –130 Pa for PtTFPP/poly(TMSP). The reference pressure P_{ref} of each datum is set at 1.0×10^{-2} Pa, which is the lower limit of the pressure range.

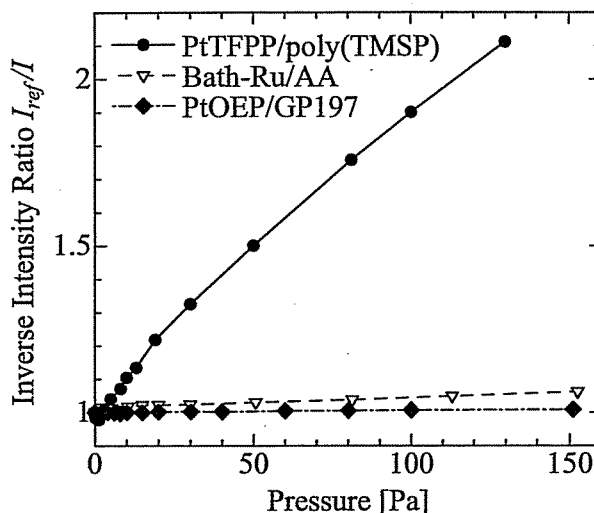


Figure 2 Stern-Volmer Plots of PtOEP/GP197, Bath-Ru/AA, PtTFPP/poly(TMSP)

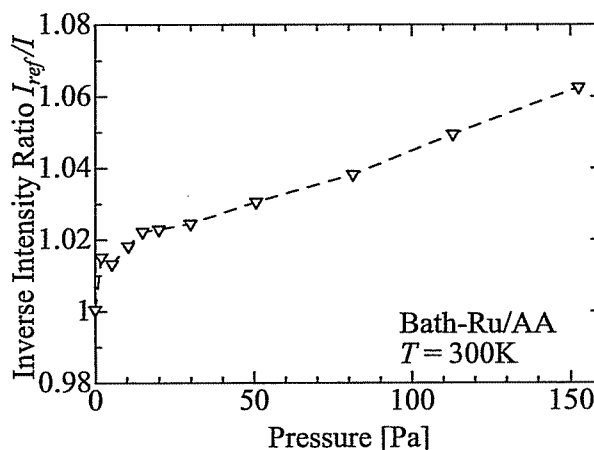


Figure 3 Stern-Volmer Plots of Bath-Ru/AA

It is clearly seen from Fig. 2 that the luminescence intensity of PtOEP/GP197 changes hardly in the range of pressure below 150 Pa, and it has little pressure sensitivity deduced from the slope of the Stern-Volmer plot. The result is attributed to insufficient gas permeability of the polymer GP197 used as the binder, so that oxygen molecules almost never diffuse into the binder and quench the luminescence of PtOEP. This result indicates that PtOEP/GP197 is not suitable for pressure measurement in the low pressure range below 150 Pa.

The inverse luminescence intensity ratio I_{ref}/I of Bath-Ru/AA depends linearly on the pressure ratio P/P_{ref} at the pressure above 20 Pa, but the nonlinear dependence appears below 20 Pa, as shown in Fig. 3. The nonlinearity is probably caused by adsorption of oxygen molecules on the anodized aluminum surface. The relatively high pressure-sensitivity of Bath-Ru/AA even in the low pressure conditions seems to be due to

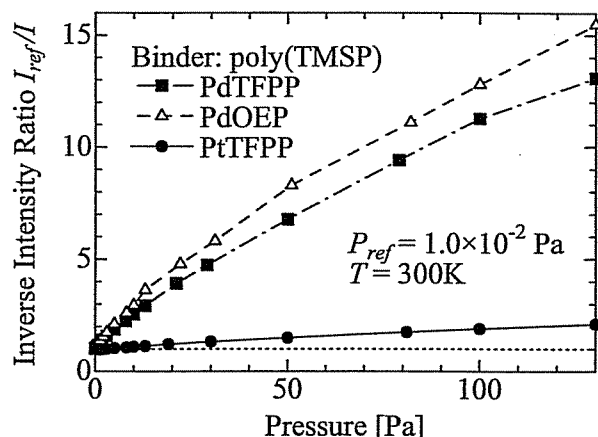


Figure 4 Stern-Volmer Plots for PSPs consisting of porphyrin and poly(TMSP)

the quenching mechanism, namely that the Bath-Ru molecules adsorbed on the anodized surface interact directly with oxygen molecules. On the other hand, the nonlinear dependence makes the calibration of Bath-Ru/AA difficult. Moreover, the hysteresis of luminescence intensity is found, which is caused by adsorption and desorption of oxygen molecules inside the pores of the anodized aluminum layer. For the reasons, it is possible to use Bath-Ru/AA only for qualitative measurements in a low-pressure region.

PtTFPP/poly(TMSP) shows the highest pressure-sensitivity among the three types of PSPs examined in this study and the good linearity of the Stern-Volmer plot over the whole range of pressure. It should also be mentioned that the absolute luminescence intensity of PtTFPP/poly(TMSP) is the highest among the three types of PSPs, resulting in the highest signal-to-noise ratio (S/N). We think such properties are due to the large free volume⁶ of poly(TMSP), unlike GP197, so that oxygen molecules can permeate more easily through polymer matrix.

PSPs consisting of porphyrin and poly(TMSP)

Figure 4 shows the Stern-Volmer plot of PSPs using poly(TMSP) as a binder. In this study, we tested three kinds of luminophore. One is PtTFPP tested in the previous section, and the others are palladium porphyrins, PdOEP and PdTFPP. The temperature T and the reference pressure P_{ref} are kept at 300 K and 1.0×10^{-2} Pa, respectively.

As easily seen in the figure, Both PdOEP/poly(TMSP) and PdTFPP/poly(TMSP) have extremely high pressure-sensitivity in the low pressure condition below 150 Pa. The Stern-Volmer coefficients A_1 of PdOEP/poly(TMSP) and PdTFPP/poly(TMSP) are obtained as 0.16 and 0.13, respectively, both of which are about 10 times larger than that of PtTFPP/poly(TMSP), 0.012. It should be noted that,

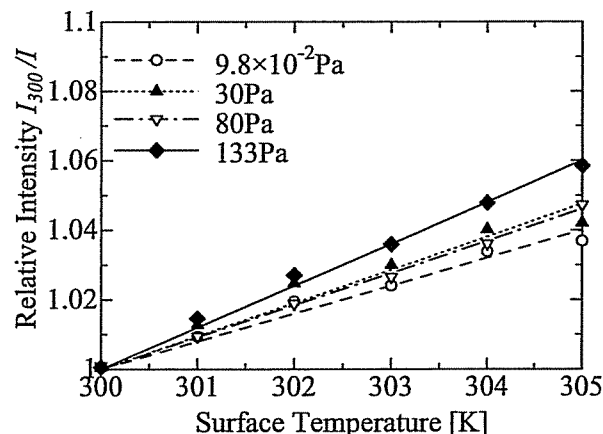


Figure 5 Temperature dependence of luminescence intensity of PtTFPP/poly(TMSP)

however, the absolute luminescence intensity of both PdOEP and PdTFPP is very low at the pressure above 10 Pa, leading to low signal-to-noise ratio (S/N). For example, the luminescence intensity of them measured by the CCD camera is comparable to the level of the dark current at 100 Pa. Therefore, PdOEP/poly(TMSP) and PdTFPP/poly(TMSP) should be applied only in very low pressure condition below 10 Pa, but they become very powerful tools in the range. On the other hand, PtTFPP/poly(TMSP) has high luminescence intensity and S/N even above 100 Pa, and it can be used in the wider pressure range than the PSPs using palladium porphyrins.

Dependence of luminescence intensity on temperature at very low pressure

Since the luminescence intensity of PSPs depends not only on partial pressure of oxygen gas but also temperature, fluctuation of temperature may cause an error in pressure measurements. In this section, we describe the temperature dependence of the luminescence intensity for Bath-Ru/AA and PtTFPP/poly(TMSP).

The dependence of the luminescence intensity on the surface temperature of the PSP samples is measured by changing the surface temperature of the PSP sample in the range of 300–305 K by 1 K step, at the oxygen pressure of 9.8×10^{-2} Pa, 30 Pa, 80 Pa, and 133 Pa.

Figure 5 shows the temperature dependence of the luminescence intensity of PtTFPP/poly(TMSP) for the four pressure conditions. In Fig. 5, the vertical axis is the relative luminescence intensity (I_{300}/I) normalized by the intensity at 300 K (I_{300}) in each pressure and the horizontal axis is the surface temperature. Lines depicted in Fig. 5 are obtained by the method of least squares to pass through the point of I_{300}/I at 300 K. In Fig. 5, only the result for PtTFPP/poly(TMSP) is depicted, but we also carried out the same experiments

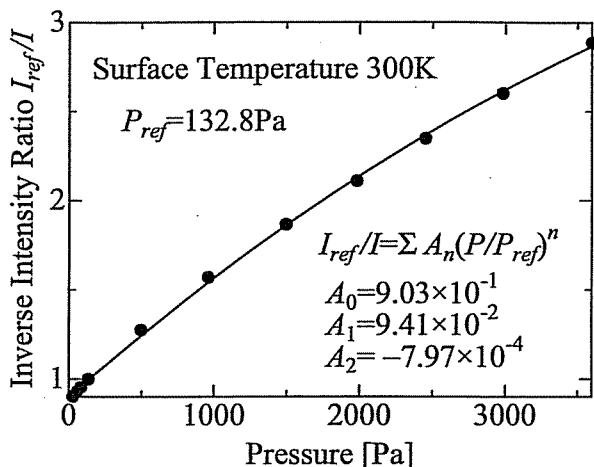


Figure 6 Stern-Volmer plot in the wide pressure range for PtTFPP/poly(TMSP)

for Bath-Ru/AA. The result for Bath-Ru/AA shows almost the same tendency and magnitude of temperature dependence as PtTFPP/poly(TMSP).

The results shown in Fig. 5 indicate the fact that the luminescence intensity decreases as temperature increases, and the higher the pressure, the larger the temperature sensitivity (i.e., the slope). This is because k_1 and D_Q [and consequently k_D and k_Q] increase as an increase in temperature, leading to a decrease in the luminescence intensity. It is also found from Fig. 5 that the higher the pressure, the larger the rate of decrease in the luminescence intensity. It seems that this result is caused by the rate constant k_Q [see Eq. (1)] which depends complicatedly on both the oxygen pressure and the surface temperature. Since the temperature dependence of the luminescence intensity is not negligibly small as evidenced in Fig. 5, we think the correction for the surface temperature is necessary for precise pressure measurements using PSP.

Measurement of Pressure Distribution on a Solid Surface Interacting with a Supersonic Free Jet

As an application of PSP to low density gas flows, we measure the pressure distribution of a solid surface interacting with a supersonic free jet. PtTFPP/poly(TMSP) is adopted for the measurement, because it has large sensitivity and high S/N over a wide range of the pressure, as mentioned above. In the experiment, a sonic nozzle is attached at the supply port of oxygen gas and temperature of the solid surface is kept at 300 K.

Fig. 6 is the Stern-Volmer plot of PtTFPP/poly(TMSP) at 300 K in the pressure range of 9.3 Pa–3.6 kPa, which is used for the calibration. The reference luminescence intensity I_{ref} is measured at $P_{ref} = 132.8$ Pa. The solid curve is obtained by the least-square fitting with the second-order Stern-Volmer equation (Eq. (5) with

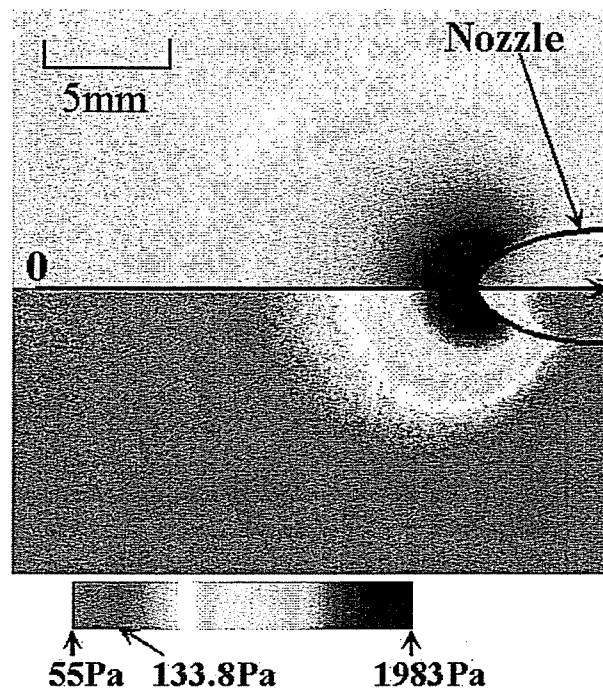


Figure 7 Pressure distribution and a pseudo-color on a solid surface interacting with an impinging supersonic free jet using PtTFPP/poly(TMSP)

$N = 2$) and the Stern-Volmer coefficients A_n are deduced as $A_0 = 9.03 \times 10^{-1}$, $A_1 = 9.41 \times 10^{-2}$, and $A_2 = -7.97 \times 10^{-4}$.

The upper part of Fig. 7 is the output of the CCD camera of the solid surface on which a supersonic free jet impinges, and the lower part the pseudo-color image of the pressure distribution estimated from the Stern-Volmer plot of Fig. 6. In Fig. 7, the source pressure of the jet and the background pressure in the chamber are set at 53.9 kPa and 133.8 Pa (pressure ratio = 403), respectively. The nozzle diameter is 0.3 mm, the impinging angle is 60° , and the distance from the nozzle exit to the surface is 2 mm. We have not compensated for local fluctuation of the surface temperature caused by the jet impingement, because the density of the jet is low.

In the same geometrical condition as Fig. 7, the luminescence intensity distributions are imaged at the various background pressures (133.8 Pa, 80.2 Pa, 50.9 Pa and 31.2 Pa) and the surface pressure distributions along the projection line of the centerline of the impinging jet are estimated as shown in Fig. 8. The horizontal axis of Fig. 8 is the distance from the origin normalized by the whole length of the projection line depicted in Fig. 7, and the origin is placed at the end of the downstream side. As shown in Fig. 8, the pressure far from the nozzle exit is close to the background pressure in every case. The results indicate the feasibility of quantitative measurement technique of the surface pressure using PtTFPP/poly(TMSP) even in

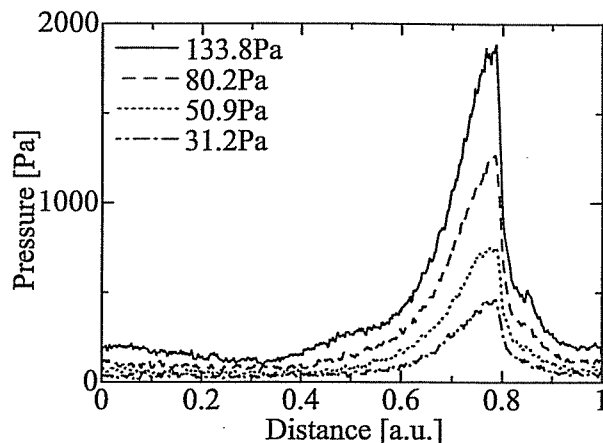


Figure 8 Pressure distribution along a centerline of a solid surface interacting with a supersonic free jet using PtTFPP/poly(TMSP)

the low pressure range.

We have also tried to measure the pressure distribution on the surface using Bath-Ru/AA, but the measured pressure far from the nozzle exit did not coincide with the background pressure, although qualitative pressure distribution map could be obtained. It is confirmed that quantitative measurements are impossible using Bath-Ru/AA.

SUMMARY

We have examined the fundamental properties of several types of PSPs in low pressure conditions below 150 Pa, to clarify the feasibility of PSP for measurement of surface pressure in the high Knudsen number flows. The concluding remarks are as follows:

1. PtOEP/GP197, which is one of the first generation of the PSPs, has little pressure sensitivity deduced from the slope of the Stern-Volmer plot in the range of pressure below 150 Pa, attributed to insufficient gas permeability of the polymer GP197 used as the binder.
2. Bath-Ru/AA shows the linearity of the Stern-Volmer plot in the range of pressure above 20 Pa, but it appears the strong nonlinearity below 20 Pa. The nonlinearity seems to be attributed to the adsorption and desorption of oxygen molecules inside the pores of the anodized aluminum layer. Moreover, Bath-Ru/AA could not be expected to measure the pressure distribution on solid surfaces quantitatively in the low pressure range.
3. PSPs using a glassy polymer poly(TMSP) as a binder have high sensitivity in the low pressure range. This is attributed to the high oxygen permeability of the poly(TMSP).

4. PdOEP/poly(TMSP) or PdTFPP/poly(TMSP) have very large Stern-Volmer coefficients, resulting in extremely high pressure sensitivity. However, their luminescence intensity is very low at the pressure above 10 Pa, and the signal-to-noise ratio is low. Therefore, the PSPs are very useful for measurements at the low pressure, although they cannot be used at the pressure above 10 Pa. On the other hand, PtTFPP/poly(TMSP) has lower Stern-Volmer coefficients than the other PSPs, but it can be used in the wider pressure range.
5. Pressure distribution on a solid surface interacting with a supersonic free jet has been measured using PSPs, showing usefulness of PtTFPP/poly(TMSP) and difficulty of Bath-Ru/AA in measurements of quantitative pressure distribution in the low pressure range.

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