Pressure Sensitive Paint Suitable to High Knudsen Number Regime

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Abstract. Pressure sensitive paint (PSP) techniques have the capability to be applied to high Knudsen number flows, such as low density gas flows, micro-flows, and so on. In this study, to inspect the feasibility of PSP for measurement of pressure on a solid surface in high Knudsen number flows, fundamental properties of PSPs are examined especially in the range of pressure below 130 Pa (about 1 Torr). As a result, it is clarified that the PSP using poly(TMSP) as a binder and using PdOEP or PdTFPP as a luminophore has very high sensitivity to oxygen pressure in low pressure conditions below 130 Pa. Pressure sensitivity to nitrogen monoxide is also examined for the above PSPs, and it is clarified that PdTFPP bound by poly(TMSP) has very high sensitivity while PdOEP has very low sensitivity to nitrogen monoxide. The combination of the PdTFPP-based PSP and NO-LIF technique enables composite measurement of flow field structures and surface pressure in high-Kn regime.

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1. Introduction

Experimental analyses of thermo-fluid phenomena with high Knudsen number, related to low density gas flows or micro/nano-technologies, need measurement techniques based on atoms or molecules, such as emission and absorption of photons. However, the measurement techniques are behind in development compared with molecular simulation techniques. For example, in the case of gas flows inside micro- and nano-systems, measurement of surface pressure has almost never been reported and development of the measurement techniques has been eagerly anticipated.

Recently the pressure sensitive paint (PSP) technique has actively developed to measure two-dimensional pressure distributions on solid surfaces [1–5]. Generally, pressure range of PSPs has been limited above 1 Torr (133 Pa), and there have been no applications to the lower pressure range other than those by the authors [4, 5], because the pressure sensitivity of PSPs seemed to be not so high in the range. Because PSPs utilize quenching of luminescence by oxygen molecules, however, it seems suitable for analyses of high Knudsen number flows, which require diagnostic tools in the molecular level.

The sensitivity of PSPs depends mainly on the quenching probability of the luminophore as well as the oxygen permeability of the binder. In this study, several kinds of luminophores and binders are investigated to select suitable combinations of luminophores and binders for measurements in low pressure conditions. The fundamental properties of the PSPs such as pressure sensitivity and temperature dependence of luminescence intensity were examined in the pressure range lower than 1 Torr.

The combination of flow visualization by LIF and surface pressure measurement by PSP is useful for detailed analyses of flow fields with high Knudsen number. For example, Niimi et al. [6] and Taniguchi et al. [7] reported the experimental analyses of linear aerospike nozzles with small dimensions by LIF and PSP. However, they used different kinds of the test gases for the two measurement techniques; while oxygen gas is used for PSP, they adopted nitrogen monoxide for LIF (NO-LIF), because NO emits much stronger fluorescence than oxygen. Engler et al. reported [2] that nitrogen monoxide can quench luminescence of PSP, but the fundamental properties such as pressure sensitivity to nitrogen monoxide have not been clarified. We have investigated the pressure sensitivity of the PSPs against nitrogen monoxide, to clarify the feasibility of the composite measurement of flow field structure by NO-LIF and surface pressure by PSP, using nitrogen monoxide as a test gas for the both measurement techniques.

2. Luminescence Properties of PSP

The pressure measurement technique using PSP is based on oxygen quenching of luminescent molecules [2, 3]. A PSP is composed of luminescent molecules and a binder material to fix the luminescent molecules to a solid surface. When the PSP is irradiated by UV light, the luminescent molecules at the ground singlet state are excited by absorption of photon energy to a higher singlet state. After the transition of the excited molecules from the singlet state to the lowest triplet state by an intersystem crossing, the molecules emit phosphorescence and transfer to the ground singlet state. Because the transition between the triplet state and the singlet state is spin forbidden, the lifetime of the phosphorescence is long. Oxygen molecules, whose ground state is triplet, can quench the excited luminescent molecules at the triplet state. As a result, the phosphorescence intensity decreases as an increase in partial pressure of oxygen. The details of quenching mechanisms of excited luminescent molecules at the triplet state by ground-state triplet oxygen are mentioned by Schweitzer and Schmidt [8] in detail. They also mentioned the enhancement of the intersystem crossing, that is, triplet oxygen can convert the excited singlet state of luminescent molecules to the triplet state.

Luminescence quantum yield Φ of PSP is given by [3]

$$\Phi = \frac{I}{I_\mathrm{a}} = \frac{k_\mathrm{L}}{k_\mathrm{L} + k_\mathrm{D} + K_\mathrm{Q}[\mathrm{O_2}]} = K_\mathrm{L}\tau, \tag{1}$$

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. $[\mathrm{O_2}]$ is the concentration of oxygen molecules, and τ the lifetime of an excited luminescent molecule.

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

$$\begin{aligned}\frac{I_0}{I} = \frac{k_\mathrm{L} + k_\mathrm{D} + K_\mathrm{Q}[\mathrm{O_2}]}{k_\mathrm{L} + k_\mathrm{D}} &= 1 + \frac{K_\mathrm{Q}[\mathrm{O_2}]}{k_\mathrm{L} + k_\mathrm{D}} \\ &= 1 + K_\mathrm{Q}\tau_0[\mathrm{O_2}],\end{aligned} \tag{2}$$

where τ_0 is the lifetime of an excited molecule in the absence of oxygen molecules. The concentration $[\mathrm{O_2}]$, the partial pressure of oxygen gas $P_{\mathrm{O_2}}$, and the total pressure P follow the relation $[\mathrm{O_2}] \propto P_{\mathrm{O_2}} \propto P$, according to Henry's law. Because K_Q and τ_0 depend on the temperature T, equation (2) can be put in a form

$$I_0/I = 1 + K(T)P, \tag{3}$$

where K is a constant depending on T. However, it is usually difficult to measure I_0, luminescence intensity in a perfect vacuum. If the luminescence intensity I_ref at the known reference pressure P_ref is obtained, the modified equation

$$\frac{I_\mathrm{ref}}{I} = A_0 + A_1\frac{P}{P_\mathrm{ref}} \tag{4}$$

can be used for the calibration. Here I_ref is the luminescence intensity at the known reference pressure P_ref. A_n are the constants called as Stern-Volmer coefficients determined by calibration tests.

The luminescence intensity I of the ideal PSP depends inversely on P following to equation (4), but the actual PSPs have nonlinear dependence of I^{-1} on P. Therefore, the following equation considering the nonlinearity should be employed:

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

In practice, a second-order polynomial ($N = 2$) is commonly used. Since the coefficients A_n depend on temperature, the effect of the temperature must be eliminated for precise measurements.

3. Experimental Apparatus

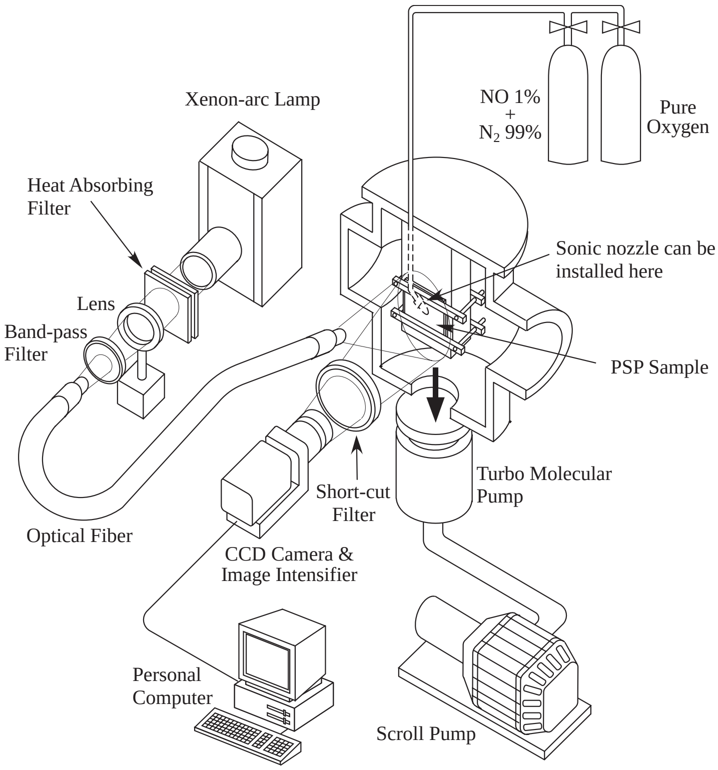


Figure 1. Experimental Apparatus

Figure 1 shows the experimental apparatus composed for this study. All of the PSPs tested in this study are applied to aluminum plates (50 mm × 25 mm) and the plates are set inside a vacuum chamber evacuated by a scroll pump (ULVAC DVS-631) and a turbo molecular pump (ULVAC UTM-300). Pure oxygen gas is supplied into the chamber, and the pressure in the chamber is monitored by a capacitance manometer and an ionization vacuum gauge. A gas mixture of NO 1% + N_2 99% can be supplied instead of oxygen. The temperature of the PSP sample is controlled by a Peltier thermo-controller and is monitored by a thermocouple. A xenon-arc lamp with a band-pass filter (400 ± 20 nm) is used as an excitation light source irradiating the sample via an optical fiber. The luminescence is filtered by a short-cut filter (600 nm) to eliminate the light from the xenon lamp, and is detected by a CCD camera (Hamamatsu C4742-95, 1280×1024 pixels, 12 bit) with an image intensifier (Hamamatsu C7970-01). The image of the luminescence is processed by a personal computer.

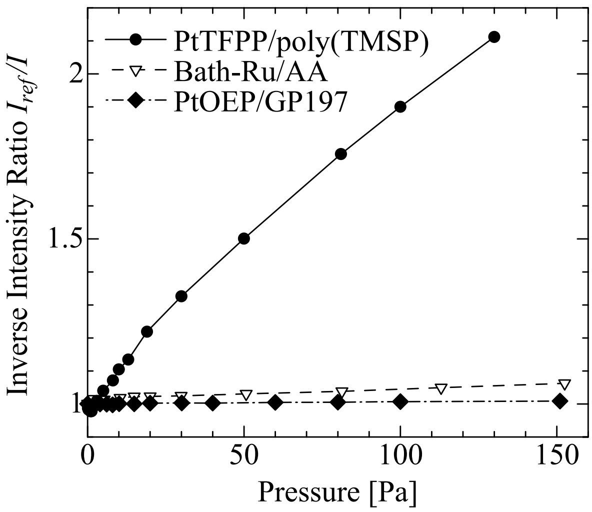


Figure 2. Stern-Volmer Plots of PtOEP/GP197, Bath-Ru/AA, PtTFPP/poly(TMSP)

4. LIST OF PSP

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

One of the PSPs is composed of Bath-Ru ⟨Ruthenium II tris(4,7-diphenyl-1,10-phenanthrolin) chloride⟩ adsorbed on a porous surface of anodized aluminum (AA). Because the luminophore Bath-Ru is exposed to the atmosphere, Bath-Ru/AA has fast response time and high sensitivity to oxygen pressure even in a cryogenic conditions [9,10]. However, it can be applied only to aluminum or aluminum alloys. The sample of Bath-Ru/AA were prepared referring to Sakaue's procedure [11].

The others utilize poly(TMSP) ⟨poly[1-(trimethylsilyl)-propyne]⟩, a glassy polymer with extremely high oxygen permeability, as a binder. This type of the PSPs are painted by using an airbrush. We applied a platinum porphyrin, PtTFPP ⟨platinum tetrakis(pentafluorophenyl) porphyrin⟩, and two palladium porphyrin, PdOEP ⟨palladium octaethylporphyrin⟩ and PdTFPP ⟨palladium tetrakis(pentafluorophenyl) porphyrin⟩, as luminophores bound by poly(TMSP). It is reported [10] that PSPs using poly(TMSP) as a binder have 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 in the University of Washington [1].

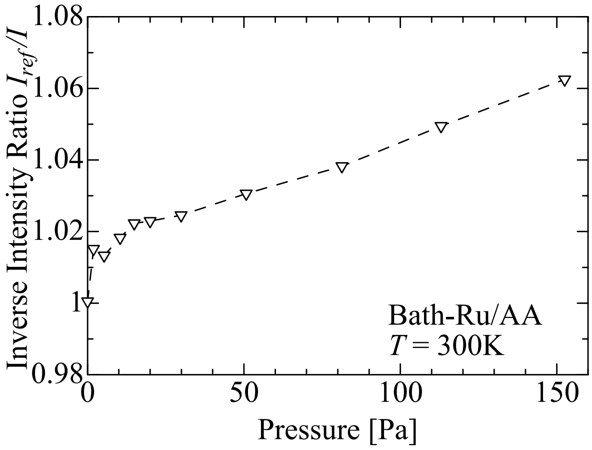


Figure 3. Stern-Volmer Plots of Bath-Ru/AA

5. Results and Discussions

5.1. Suitable Binders for Application in Low Pressure

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 of oxygen gas on the sample surface, and the vertical axis is I_{ref}/I mentioned in equation (5). The surface temperature of each sample is kept at 300 K (but PtOEP/GP197 is kept at 293 K). The pressure ranges are 1.0×10^{-2}–151 Pa for PtOEP/GP197, 1.0×10^{-2}–152.5 Pa for Bath-Ru/AA, and 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.

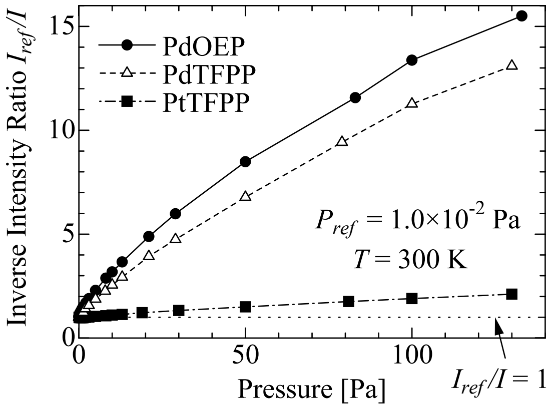
It is clearly seen from figure 2 that the luminescence intensity of PtOEP/GP197 changes hardly in the range of pressure below 150 Pa, and it has little pressure sensitivity deduced from the slope of the Stern-Volmer plot. The result is attributed to insufficient gas permeability of the polymer GP197 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 pressure sensitivity of Bath-Ru/AA in the low pressure condition is higher than that of PtOEP/GP197, but much lower than that of PtTFPP/poly(TMSP). Moreover, the nonlinear dependence on the pressure appears below 20 Pa, as shown in figure 3. The nonlinear sensitivity makes the use of Bath-Ru/AA for measurements in low-pressure regions very difficult. The nonlinearity is probably caused by adsorption of oxygen molecules on the anodized aluminum surface, and it makes the calibration of Bath-Ru/AA complicated. The alternative cause of the nonlinearity may be steric and structural effects of Bath-Ru, especially micro-heterogeneities. Bedlek-Anslow et al. [12] and Kneas et al. [13] discussed the micro-heterogeneities of ruthenium complexes resulting in low and non-linear sensitivity. Although their studies dealt with ruthenium complexes in polymer binders, the micro-heterogeneities of ruthenium complexes may occur also in anodized aluminum layer, resulting in the nonlinearity of Bath-Ru/AA and its lower sensitivity than that of PtTFPP/poly(TMSP) shown in figures 2 and 3.

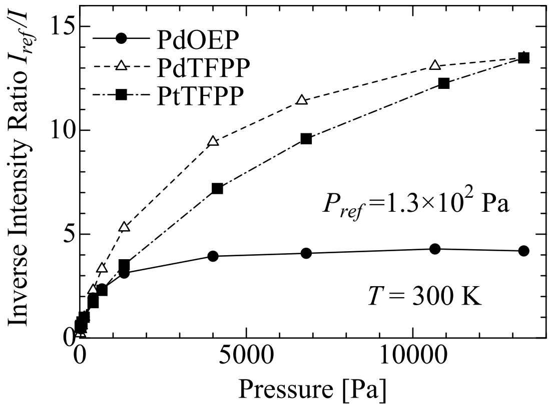
PtTFPP/poly(TMSP) shows the highest pressure-sensitivity among the three types of PSPs examined here, and it has the good linearity of the Stern-Volmer plot over the range of pressure below 130 Pa. It should also be mentioned that the absolute luminescence intensity of PtTFPP/poly(TMSP) is the highest among the three types of PSPs, resulting in the highest signal-to-noise ratio. Such properties seem to be due to the large free volume [14] of poly(TMSP), unlike GP197, so that oxygen molecules can permeate more easily through polymer matrix.

Although the Stern-Volmer plot of PtTFPP/poly(TMSP) obtained in this study did not have distinct nonlinearity, in contrast to that of Bath-Ru/AA, some studies mentioned the micro-heterogeneities of PtTFPP caused by polymers, resulting in multiexponential lifetime of the luminescence. For example, Ruyten and Sellers [16] and Mitsuo et al. [17] examined the multiexponential lifetime of PtTFPP in fluoro-isopropyl-butyl and poly-IBM-co-TFEM polymers, respectively, for simultaneous measurement of pressure and temperature, utilizing the different dependence of lifetime on pressure and temperature. It may be useful to analyze the multiexponential lifetime of PtTFPP/poly(TMSP) for simultaneous measurement of pressure and temperature.

5.2. Sensitivity of PSPs consisting of porphyrin and poly(TMSP)



(a) in low pressure condition



(b) in high pressure condition

Figure 4. Stern-Volmer plots of PSP using poly(TMSP) as a binder

As mentioned in the previous section, PtTFPP/poly(TMSP) has very high pressure sensitivity in low pressure range below 130 Pa, because of high oxygen permeability of poly(TMSP). However, it is reported that palladium porphyrins have higher oxygen sensitivity than platinum porphyrins [15]. In this study, three luminophores are combined with poly(TMSP), and the sensitivity of the PSPs are examined. One is PtTFPP, a platinum porphyrin examined in the previous section, and the others are palladium porphyrins, PdOEP and PdTFPP.

Figure 4 shows the Stern-Volmer plot of PSPs using poly(TMSP) as a binder against oxygen pressure in static pure oxygen. For figure 4(a), the pressure range is from 1.0×10^{-2} Pa to 1.3×10^2 Pa, and the reference pressure P_{ref} was set at 1.0×10^{-2} Pa. For figure 4(b), the pressure range is 1.0×10^2–1.3×10^4 Pa, and $P_{\text{ref}} = 1.3 \times 10^2$ Pa. The surface temperature T was kept at 300 K in the both cases. As easily seen in figure 4(a), PSPs using the palladium porphyrins, PdOEP and PdTFPP, have extremely high pressure-sensitivity in the low- pressure condition below 130 Pa. However, in the higher pressure range above 130 Pa the pressure sensitivity of PdOEP and PdTFPP is relatively low as shown in figure 4(b), resulting in the strong nonlinearity of the Stern-Volmer plots. Because the luminescence of both PdOEP and PdTFPP is highly quenched at the pressure above 130 Pa, the saturation of quenching occurs and the dependence of the luminescence intensity on the oxygen pressure disappears. As a result, PdOEP and PdTFPP bound by poly(TMSP) would be very powerful measurement tools in low pressure condition below 130 Pa, although they cannot be applied in the higher pressure range. The pressure sensitive luminophore suitable to pressure measurements in low-density gas has also potential for pressure measurements in micro- and nano-flows with high Knudsen number.

5.3. Sensitivity of PSPs to Nitrogen Monoxide

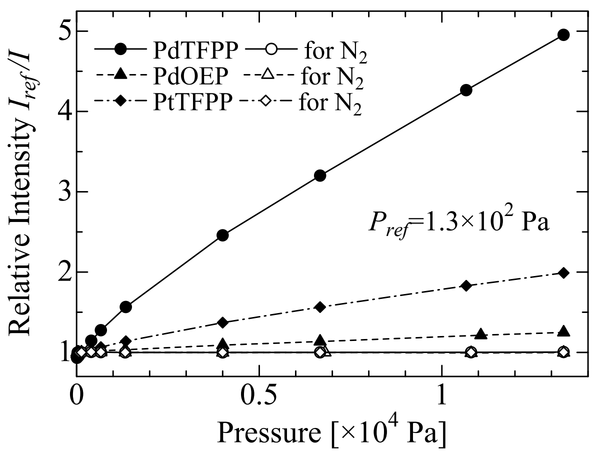


Figure 5. Stern-Volmer plots of PSP against the pressure of NO 1% + N_2 99%

Engler et al. [2] have reported that nitrogen monoxide can quench luminescence of PSP, but the fundamental properties such as pressure sensitivity against nitrogen monoxide have not been examined in detail. We have investigated the pressure sensitivity of the PSPs against nitrogen monoxide, to clarify the feasibility of the composite measurement of flow field structure by NO-LIF (Laser Induced Fluorescence) and surface pressure by PSP.

Figure 5 shows the Stern-Volmer plots of the PSPs for the pressure of gas mixture of NO 1% + N_2 99% (closed symbols) and those of pure nitrogen (open symbols). For the gas mixture, the horizontal axis does not indicate the partial pressure of nitrogen monoxide, but the total pressure of the gas mixture. As shown in figure 5, the luminescence intensity of all the PSPs tested in this study depend on the pressure of the gas mixture of NO 1% + N_2 99%, although the PSPs do not have sensitivity to pure nitrogen gas. It follows from the results that the PSPs have considerable sensitivity to nitrogen monoxide. In particular, PdTFPP has the highest sensitivity to nitrogen monoxide among the three PSPs tested in this study. The result evidenced that the combination of the PdTFPP-based PSP and NO-LIF technique enables composite measurement of flow field structures and surface pressure in high-Kn regime.

Although PdOEP has very high pressure sensitivity to oxygen, it has lower sensitivity to nitrogen monoxide than PtTFPP, which has relatively low sensitivity to oxygen. The mechanism of the quenching by nitrogen monoxide is unknown, but it is supposed from the results that the probability of the quenching caused by nitrogen monoxide depend not only on the kind of the metal ion, but also on the molecular structure of porphyrin.

6. Summary

We have examined the fundamental properties of PSPs in low pressure conditions, to clarify the feasibility of PSP for measurement of surface pressure in high Knudsen number flows. The following concluding remarks are obtained:

(i) In the low-pressure conditions below 130 Pa, PSPs using poly(TMSP) as a binder show high sensitivity. In particular, PdOEP bound by poly(TMSP) shows the highest pressure sensitivity among the three PSPs tested in this study. Although its pressure sensitivity decreases rapidly at the pressure above 130 Pa, the PSP would be very useful for measurements in low pressure conditions.

(ii) We have clarified experimentally that the PdTFPP/poly(TMSP) has the highest pressure sensitivity to nitrogen monoxide among the three PSPs tested in this study. The result evidenced that the combination of the PdTFPP-based PSP and NO-LIF technique enables composite measurement of flow field structures and surface pressure in high-Kn regime. On the other hand, PdOEP/poly(TMSP) has very low sensitivity to nitrogen monoxide, although it has very high sensitivity to oxygen.

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