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Humidity effects in the response of a porous pressure-sensitive paint

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ABSTRACT

Fast-responding pressure-sensitive paints (PSP) based on luminescent oxygen sensor have porous structure in order to improve diffusive oxygen permeation into paint layer. This porous structure inevitably works as an absorbent of moisture in air, which has considerable influences on the response of the paint. The response of anodized alumina pressure-sensitive paint (AA-PSP), which is one of common fast-responding PSPs, was characterized in moist air. Tris(4,7-diphenyl-1,10-phenanthroline) ruthenium (II) dichloride was used as luminophore. Hydrophobic coating was applied to reduce the moisture adsorption. Emission characteristics of the PSP sample were measured using a calibration apparatus, in which pressure, temperature and humidity can be controlled independently. Moisture sorption isotherm of the PSP sample was measured by volumetric gas adsorption method. The experimental results show that the emission intensity of PSP increases in proportion to the relative humidity at a constant temperature and a pressure. This humidity sensitivity remains a constant value under various temperature conditions. The pressure sensitivity has a constant value irrespective of temperature and relative humidity. Moisture adsorption isotherm of the AA-PSP exhibits that the amount of water slowly increases in proportion to the relative humidity in the range from 20% to 80%. This implies that, within this range, water molecules are adsorbed and diffuse into the pore sidewalls to form thin water layer on the pore surface, which may play a major role in humidity sensitivity of the PSP.

1. Introduction

Luminescent pressure-sensitive paint (PSP) is widely used for surface-pressure measurements in aerodynamic testing [1,2]. The PSP is a thin film consisting of photoluminescent dyes (luminophores) and a supporting matrix (binder). The sensing mechanism is the energy exchange between luminophores and oxygen molecules in the film. Oxygen molecules of the test gas diffusively permeate into the film. In a quasi-equilibrium state, the oxygen concentration is proportional to the local gas pressure immediately above the film. Therefore, this type of oxygen sensor can be utilized as a pressure sensor.

The PSP is an absolute pressure sensor. Since the emission rate is inversely proportional to the oxygen concentration in the film via Stern-Volmer relation [1], the measured luminescent intensity I is related to the absolute pressure p as

$$\frac{I_{\mathrm{ref}}}{I} = A + B\frac{p}{p_{\mathrm{ref}}}, \tag{1}$$

where I_{ref} denotes the intensity at a reference pressure p_{ref}. The constants A and B must be positive and satisfy $A+B=1$. If the pressure p is close to the reference pressure p_{ref}, the pressure difference $\Delta p\ (=p-p_{\mathrm{ref}})$ approximately satisfies

$$\frac{\Delta I}{I_{\mathrm{ref}}} = -B\frac{\Delta p}{p_{\mathrm{ref}}}, \tag{2}$$

where $\Delta p \ll p_{\mathrm{ref}}$ and $\Delta I = I - I_{\mathrm{ref}} \ll I_{\mathrm{ref}}$.

Since the constant B must be less than unity, Eq. (2) indicates that the relative intensity change $\Delta I/I_{\mathrm{ref}}$ is smaller than the relative pressure change $\Delta p/p_{\mathrm{ref}}$. This low-sensitivity imposes a serious problem on the pressure measurement in low-speed flow regime. Surface pressure distribution around a body in incompressible flow is characterized by the dynamic pressure $q=\rho U^2/2$ where ρ denotes the density of gas and U the characteristic speed of the flow. For a low-speed flow in atmospheric air, e.g. $\rho \sim 1.2\,\mathrm{kg/m^3}$ and $U=O(10\,\mathrm{m/s})$, the dynamic pressure q is within the order of 1 kPa. This value is much smaller than atmospheric pressure, e.g. about 100 kPa, which must be the reference pressure p_{ref}. Therefore, accurate characterization is needed to apply the PSP to low-speed aerodynamic testing, because the pressure must be determined using such a small difference of the intensity.

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Fast-responding PSP is available on unsteady flow measurement [3,4]. Time response of fast-responding PSP is less than 1 ms, which enable us to measure various aerodynamic phenomena such as shock waves, flow around rotating machinery and pressure fluctuation due to turbulent flows.

The fast-responding PSP has a porous structure in order to improve gas diffusivity in the paint layer, which is a major parameter governing the time response of the PSP [5–7]. Thin-layer chromatography (TLC) plate [8], anodized alumina [6,9–11], and polymer/ceramic composite [12,13] are common materials for fast-responding PSP. These materials are made by metal oxides such as SiO_2, Al_2O_3 and TiO_2.

Sakaue et al. [14] showed the existence of water in a test gas has substantial influences on the response of anodized alumina PSP (AA-PSP). For example, the intensity of emission signal under humid air is larger than that under dry air. They also showed that such an influence was reduced by hydrophobic coating using alkanoic acids.

In room temperature condition, the surface of the metal oxides without special surface modification exhibits hydrophilic nature due to chemically adsorbed hydroxyl group onto the surface [15]. Especially, the anodized alumina contains a certain amount of electrolyte anions [16]. Even in a low humidity regime the presence of these anions on the pore surface provides a high charge density for easy physisorption of water molecules [17]. Therefore porous metal oxides are effective absorbents of moisture in air. The materials similar to fast-responding PSP are applied to measure relative humidity and moisture content [18]. However, sufficient knowledge has not revealed on the effect of humidity on the response of fast-responding PSPs.

In this paper, we characterize the response of AA-PSP in moist air. We focus our attention to the characteristics of AA-PSP close to atmospheric pressure, room temperature and moderate humidity, because we aim to use the AA-PSP in low-speed flow applications in room air. In order to evaluate the effect of humidity on the emission characteristics in detail, we newly equipped a calibration apparatus, in which pressure, temperature and humidity can be controlled independently. We measured moisture sorption isotherm of the PSP sample by using another equipment, which provides good information to understand the role of water content in the porous layer on the PSP signal.

2. Experiments

2.1. Fabrication of AA-PSP

We fabricated the sample of anodized alumina PSP according to the procedure described by Sakaue et al. [10] and Kameda et al. [6]. Hydrophobic coating using *n*-alkanoic acid was also applied by a modified procedure based on Sakaue et al. [14]. Schematic diagram of anodized alumina PSP with a microscope image is shown in Fig. 1. Anodized alumina has cylindrical mesopores whose sidewalls are parallel to each other [16]. Pressure (oxygen) sensitive luminophore is adsorbed on the surface of mesopores via physical or chemical bonding. Lipophilic hydrocarbon group in the alkanoic acid is covered over the alumina, because hydrophilic carboxyl group in the alkanoic acid is bonded with anions (OH^- and SO_4^{2-}) on the anodized alumina.

We used a 1-mm-thicknees plate of aluminum alloy containing Mg, Fe, Cr, and Si (Japanese Industrial Standards (JIS) A5052) as the starting material of the sample. The plate cut into 100 mm×80 mm was anodized at a constant current density of 12.5 mA/cm^2 in a dilute sulfuric acid (1 mol l^{-1}) at a constant temperature of 10°C. After 20 min of anodization, subsequently, chemical etching was conducted in 3 wt% phosphoric acid for 20 min at a constant temperature (30°C). Finally, we obtained the anodized alumina layer with a thickness of 10 μm and a mesopore diameter of 20 nm [6].

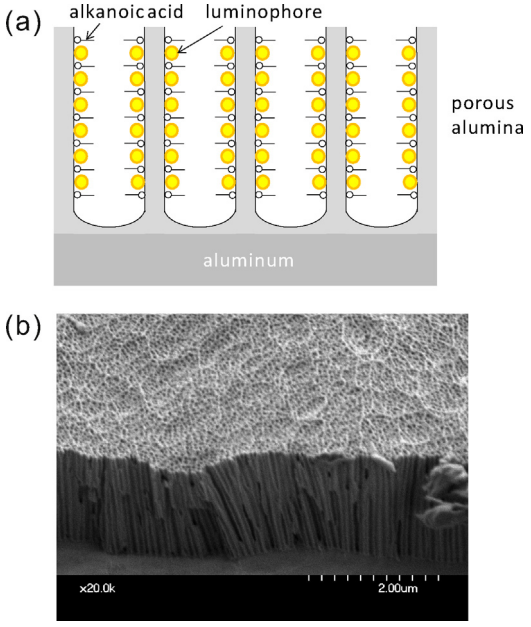

Fig. 1. Hydrophobic anodized alumina PSP. (a) Schematic diagram of adsorption of luminophore and alkanoic acid. (b) Image of the porous structure of anodized alumina taken by a field-emission scanning electron microscope (FE-SEM, Hitachi S-4700).

The luminophore was tris(4,7-diphenylphenanthroline) ruthenium(II) dichloride ($[Ru(dpp)_3]Cl_2$, Frontier Science). The alkanoic acid was stearic acid ($CH_3(CH_2)_{16}COOH$). The luminophores and the alkanoic acid molecules are separately adsorbed on the anodized alumina via dipping method. The aluminum plate was dipped firstly in the dye solution, then in the alkanoic acid solution.

The solvent of dye solution was dichloromethane. The concentration of the dye was 0.6×10^{-3} mol l^{-1}. Ten-seconds dipping was conducted twice at 20°C. In order to remove excessive luminophores from the surface, the sample was rinsed with dichloromethane. It was dried well in a vacuum dryer during 24 h.

Subsequently, the dye-adsorbed sample was dipped in the stearic acid solution, in which stearic acid was dissolved in hexane with 5×10^{-3} mol l^{-1}. Twenty-four hours dipping was conducted at 20°C. Finally, the sample was rinsed with hexane then it was dried well in the vacuum dryer.

2.2. Pressure, temperature and humidity sensitivity test

In order to characterize the effect of humidity very carefully, we equipped a new calibration apparatus in which pressure, temperature and humidity can be controlled separately. Schematic diagram of the calibration apparatus is shown in Fig. 2. The apparatus consists of a large thermo-hygrostat chamber (Espec PR-3J), a pressure chamber, and an optical setup. The pressure chamber and the optical setup were installed in the thermo-hygrostat chamber. The PSP sample was placed directly on the bottom plate of the pressure chamber.

The pressure chamber is a cylindrical aluminum vessel whose top is sealed by a flat optical glass. When we measured the temperature and humidity sensitivity at a constant pressure, the pressure chamber was opened thus temperature and relative humidity around the sample were equivalent to those in the thermo-hygrostat chamber. The pressure chamber was sealed when we