Short communication

Hydrophilic and hydrophobic TiO\(_2\) coatings by pulsed electrophoretic deposition

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Abstract

Hydrophobic and hydrophilic coatings have been widely studied because of their functions such as anti-corrosion and self-cleaning. In this study two different TiO\(_2\) suspensions, obtained by dispersing of hydrophilic and hydrophobic TiO\(_2\) particles in ethanol, were used for preparation of titania coatings on stainless steel substrates by pulsed electrophoretic deposition (EPD). The resultant hydrophilic and hydrophobic rutile TiO\(_2\) coatings showed random orientation and are dense with no cracks. The thicknesses of the coatings obtained using hydrophilic and hydrophobic TiO\(_2\) particles were 22.5 and 20.1 µm, respectively, whereas their contact angles were 6.3° and 124.0°, respectively. The results show that hydrophilic and hydrophobic TiO\(_2\) coatings can be performed using pulsed EPD.

Keywords: coating, electrophoretic deposition, hydrophilic, hydrophobic, TiO\(_2\)

I. Introduction

Hydrophilic coatings have been investigated intensively because of their potential for improvement of heat transfer [1], self-healing anti-corrosion [2], low friction [3] and self-cleaning [4,5]. Hydrophobic coatings have attracted technological interest because of specific properties when applied for anti-icing [6,7], anti-fogging [8], anti-corrosion [9] and self-cleaning [10]. For these reasons, hydrophilic and hydrophobic coatings are attracting attention as useful means of protecting and functionalizing material surfaces.

Hydrophilic and hydrophobic coatings are usually obtained by plasma treatment of the surface [6,11,12] and deposition of organic and inorganic layers by different methods [1–5,7–10]. Practical use requires technique which enables deposition of hydrophilic and hydrophobic coatings onto substrate with a large area or a curved substrate. Electrophoretic deposition (EPD) is a method by which one can easily coat a large area or curved materials, although the substrate must be electrically conductive [13–16]. We already used pulsed electrophoretic deposition to fabricate LiCoO\(_2\) electrodes for Li ion batteries [15] and radiative cooling Si\(_3\)N\(_2\)O devices [16] on stainless steel substrates. Pulsed EPD is a method by which various particles can be easily, homogeneously and densely coated onto conductive substrates [14–16].

In this study, the idea was to prepare hydrophilic and hydrophobic TiO\(_2\) coatings using pulsed EPD method. Earlier reports have described that desirable aqueous TiO\(_2\) suspension can be produced if the pH is low [17]. On the other hand, in the present investigation we used ethanol as the medium and controlled the hydrogen ion concentration in the ethanol by adding hydrochloric acid in accordance to earlier report [17]. Thus, hydrophilic and hydrophobic TiO\(_2\) particles were used as starting materials and corresponding suspensions were coated onto a stainless steel substrate using pulsed EPD method. The hydrophilicity and hydrophobicity of the coatings were evaluated by measurement of the contact angle.

II. Experimental procedure

Hydrophilic TiO\(_2\) powder (rutile TiO\(_2\) particles, JR-405; TAYCA Corp, Japan) and hydrophobic TiO\(_2\) pow-
(silicone-based hydrophobic coating onto rutile TiO$_2$ particles, R Y -405, T A YCA Corp.) were used as starting materials. These powders (in concentration of 0.5 wt.%) were dispersed into 80 ml of ethanol by adding of 0.04 ml of hydrochloric acid. The powders were dispersed via supersonic agitation for 5 min and stirred for 1 h to prepare suspensions.

Titania coating was deposited by immersing of stainless steel substrate in the previously prepared suspension and application of pulsed-DC electrical bias. The pulsed-DC electrical bias (square wave) was applied to the stainless steel electrodes (substrates) at 1 kHz with an alternating bias voltage of 0 or $-20$ V using a universal source (HP-3245A; Agilent Technologies Inc, USA) for 5 min. After coating, the substrate with deposited layer was removed from the suspension. Thermal treatment was carried out at 300 °C for 30 min in the case of the hydrophilic TiO$_2$ coating and 100 °C for 30 min for the hydrophobic TiO$_2$ coating (to protect the silicone film present on the TiO$_2$ particle surface).

Crystal structure of the deposited coatings was confirmed using an X-ray diffractometer (XRD, 30 kV, 15 mA, Rigaku Miniflex; Rigaku Corp, Japan) with Cu Ka radiation. Size and morphology of the starting TiO$_2$ particles were characterized using a transmission electron microscope (TEM, EM-002B; Topcon Corp, Japan), where each TiO$_2$ suspension was dropped onto a copper TEM grid and subsequently dried. Microstructure of the coatings was observed using a scanning electron microscope (SEM, JCM-6000 Plus; JEOL Ltd, Japan) and contact angle (between water droplet and the coating surface) was evaluated using the sessile drop technique with ionized water [18].

### III. Results and discussion

TEM images of the dispersed hydrophilic and hydrophobic TiO$_2$ particles, shown in Fig. 1, confirm that there is no significant aggregation of the TiO$_2$ particles in both suspensions. In other words, these results showed that the TiO$_2$ particles were dispersed almost entirely under the used conditions. It can also be seen that both TiO$_2$ particles had particle size of approximately 200 nm and spherical morphology.

We also tried to prepare suspensions with both starting TiO$_2$ powders using water. Aggregation was observed using the hydrophilic TiO$_2$ particles, whereas the hydrophobic TiO$_2$ particles, because of their hydrophobicity, floated on the liquid surface. Thus, suspension was not obtained when water was used. These results revealed that the ethanol is suitable solvent for preparing hydrophilic and hydrophobic TiO$_2$ suspensions.

XRD patterns of the hydrophilic and hydrophobic TiO$_2$ coatings are presented in Fig. 2. Except of the peaks attributable to the stainless steel substrate, all other XRD peaks (2θ of 27.3°, 36.0° and 54.2°) for both
coatings were assigned to rutile TiO$_2$ (JCPDS21-1272). The coatings are polycrystalline with random orientation of the grains.

Inset photographs in Fig. 2 present an overview of the coatings. Photographs show that homogeneous white coloured TiO$_2$ coatings were deposited on the stainless steel substrates.

Figure 3 presents surface and cross-sectional SEM images of both coatings. The surface and cross-sectional images of the coatings show that both coatings are very dense without cracks or pores. Thicknesses of the coatings produced using the hydrophilic and hydrophobic TiO$_2$ particles are 22.5 and 20.1 $\mu$m, respectively.

The hydrophilicity of each coating and stainless steel substrate was evaluated in terms of the contact angle. Photographs of water droplets adhering (shown in Fig. 4) confirm that the contact angles for the stainless steel substrate and the coatings obtained using hydrophilic TiO$_2$ and hydrophobic TiO$_2$ are, respectively, 97.9°, 6.3° and 124.0°. These results indicate that the coating produced using hydrophilic TiO$_2$ particles exhibited hydrophilicity, whereas the coating produced using hydrophobic TiO$_2$ particles exhibited hydrophobicity. The obtained results demonstrated that both hydrophilic and hydrophobic TiO$_2$ coatings, with sufficient thickness, on conductive stainless steel substrates can be produced using pulsed EPD.

An earlier study [19] indicated that superhydrophilicity was obtained if the contact angle is 5° or less. On the other hand, superhydrophobicity was demonstrated if the contact angle is 150° or more [20]. Furthermore, it was also reported that hydrophilicity and hydrophobicity can be improved by controlling the surface structure [21,22] or chemical surface modification [22] of a coating. In the method used in this study, we might also be able to control hydrophilicity and hydrophobicity fur-
ther by changing structure of raw material and by modifying the surface structure. Those investigations will be undertaken in the future work.

IV. Conclusions

Stable suspensions of hydrophilic and hydrophobic TiO$_2$ particles were prepared in ethanol as dispersing medium. TiO$_2$ coating was deposited by immersing of stainless steel substrate in the previously prepared suspension and application of pulsed-DC electrical bias. The obtained coatings are dense, without any cracks and have sufficient coating thickness. Coatings prepared using the hydrophilic TiO$_2$ particles showed hydrophilicity with the low contact angle of 6°, whereas the coating deposited using the hydrophobic TiO$_2$ particles indicated hydrophobicity with the high contact angle of 124°. These results demonstrate that both hydrophilic and hydrophobic TiO$_2$ coatings on conductive stainless steel substrates can be created easily using pulsed EPD.

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References