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Article

Wettability Characteristics of Laser Surface Textured Plasma Sprayed TiO_2/ZnO Coatings

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Abstract

Surface wettability behaviour is generally categorised as hydrophobic and hydrophilic depending on the contact angle value. Surface wettability has been attracting considerable attention in research due to its unique behaviour in the field of self-cleaning, anti-fouling and anti-corrosion. Surfaces with high and low wettabilities can be fabricated using various methods, including chemical etching, anodisation and laser surface texturing. The present study investigated the effects of textured surfaces via laser surface texturing on the wettability properties of TiO_2/ZnO coatings. TiO_2/ZnO coating was selected due to its high photocatalytic activity, non-toxicity and low cost, which are essential properties for self-cleaning and anti-fouling applications. Picosecond laser ablation was used to produce micro-dimple textures on the coating surfaces. The wettability of the laser-textured surfaces was greatly reduced, achieving superhydrophilic properties with contact angle of 1.4° ± 2.42° for laser-textured TiO_2 coating. On the other hand, coatings with ZnO compositions exhibited increased contact angles for both textured and non-textured surfaces. Moreover, no clear cut correlations between the surface roughness properties of non-textured and laser-textured TiO_2/ZnO coatings and the surface wettability properties was observed. This finding provides new approaches in designing textured surface materials that can effectively increase the wettability properties for self-cleaning and anti-fouling applications.

Keywords

laser surface texturing, TiO_2/ZnO coating, wettability, self-cleaning

1 Introduction

Surface wettability can be verified by evaluating the contact angle (θ) of the liquid drop over the solid surface. The contact angle is defined as the angle formed between the solid surface and the tangent drawn at the liquid drop. The wettability behaviour of surfaces is classified as hydrophobic or hydrophilic. A hydrophobic surface tends to repel water, whereas a hydrophilic surface tends to be wetted by water. A surface is considered hydrophobic if the water contact angle is $\theta > 90°$ and hydrophilic if the water contact angle is $\theta < 90°$. For superhydrophilic surfaces, θ approaches to zero value ($\theta < 10°$), and the liquid drop tends to evenly spread on the surface. Table 1 shows the relationship of contact angle values and wettability behaviour. Surface wettability has attracted considerable attention in research due to its unique behaviour in the field of self-cleaning, anti-fouling and anti-corrosion. In the self-cleaning field, the surfaces are divided into two categories: (i) hydrophilic surfaces, where water drops spread over the surface and form a water film and the contaminants on the surface are washed away during the spreading process (Fig. 1(a)), and (ii) hydrophobic surfaces, where the water drops roll off the surface quickly due to the water-repellent and low-adhesive properties of the surface, thereby removing the contaminants (Fig. 1(b)). In recent years, a great amount of work has been dedicated to design self-cleaning surfaces. Inspired by nature, especially the lotus structure, many superhydrophobic surfaces have been fabricated using photolithography [1], template [2], sol-gel techniques [3]. In addition, shark skin exhibits low drag property, which helps maintain self-cleaning property during swimming [4]. Inspired by shark skin, nanostructured hierarchical surfaces were fabricated on polypropylene, producing a hydrophilic surface [5].

The present study used laser-surface-textured TiO_2/ZnO coatings given its high photocatalytic activity, non-toxicity and low cost for self-cleaning and anti-fouling applications [6, 7]. The use of laser surface texturing or laser surface modification to produce surfaces for different applications has been extensively studied [8, 9]. Laser surface texturing involves creating different patterns on substrates and can effectively improve surface features [8, 10–12]. This method is favourable because (i) it enables the excellent control of surface roughness from the nano- to microscale without drastically changing surface composition, (ii) it is a single-step process under ambient conditions, and (iii) it is applicable with a wide range of material types [13, 14]. Therefore, the present study developed TiO_2/ZnO coatings with different ZnO contents (mass%). Dimpled structures were selected on the surfaces of coatings through laser surface texturing with a picosecond laser ablation technique. The effects of laser surface texturing on the wettability properties of TiO_2/ZnO coatings with various compositions were investigated. Dimpled patterns were produced to increase the surface area of the coating and to change the surface topographical properties of the coatings. Moreover, the effect of laser texturing process towards the surface roughness properties of TiO_2/ZnO coatings was determined.

Table 1 Relationship of contact angle values and wettability behavior

Contact angle	Wettability
$\theta > 90°$	Hydrophobic
$\theta > 150°$	Superhydrophobic
$10° < \theta < 90°$	Hydrophilic
$\theta < 10°$	Superhydrophilic

2 Experimental methods

2.1 Materials

TiO_2 powder (Metco 102 Oerlikon Metco, ≥99.0 mass%) and ZnO powder (Sigma Aldrich, ≥99 mass%) were used as raw materials. The TiO_2 powders containing 0 mass%, 10 mass% or 30 mass% ZnO contents were mixed to improve flowability and homogeneity and reconstituted as feed powders for plasma spraying. The details of the mixing process are as follows: 100 g of powder, 50 ml of deionised water and 10 ml of polyvinyl alcohol solution (5 mass%) were added into a tank, mixed by milling process for 2 h, dried at 80°C for 24 h and sieved using an 80-mesh sieve.

2.2 Sample preparation

All coatings were deposited onto 30 cm (length) × 5 cm (width) × 7 mm (thickness) carbon API steel by using an atmospheric plasma spray system with a SG-100 torch (Praxair, USA) mounted on an ABB IRB Industrial robot. Prior to deposition, the substrate was blasted with aluminium grit and ultrasonically cleaned in ethanol and deionised water. The dried substrate was plasma-sprayed under the parameters presented in Table 2. Then, areas with dimensions of 8 mm × 8 mm on the plasma-sprayed TiO_2/ZnO coatings were subjected to a laser surface texturing process using a laser Q-switched Nd:YAG picosecond laser system to create microdimpled textures on the surfaces. As illustrated in Fig. 2, the texturing technique involved covering a series of intermediate lines with several dimples by

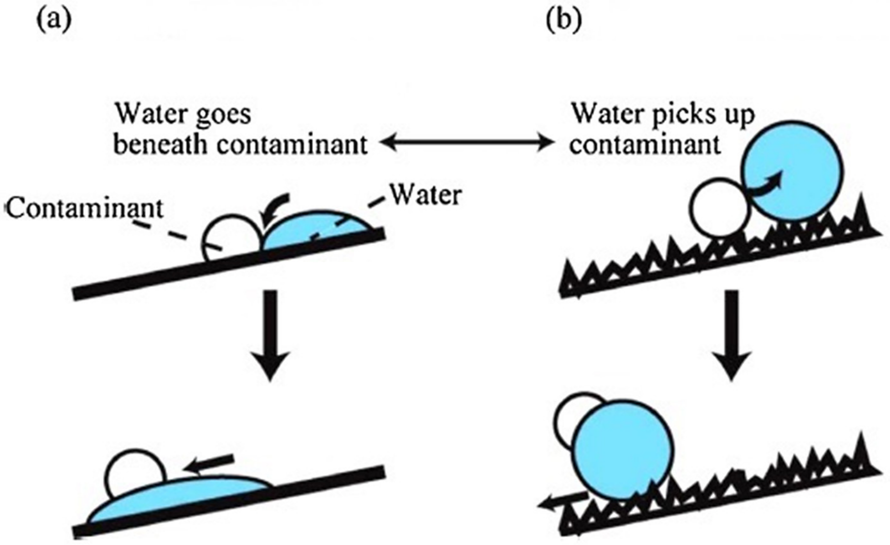

Fig. 1 Schematic representation of self cleaning process on (a) hydrophilic and (b) hydrophobic surface [6]

Table 2 Process parameters for atmospheric plasma spraying

Parameter	Value
Arc current (A)	600
Primary gas Argon (psi)	80
Secondary gas Helium (psi)	40
Carrier gas Argon (psi)	30
Powder feed rate (rpm)	4
Spraying distance (mm)	80
Robot speed (mm/s)	250
Pre heat (cycle)	2

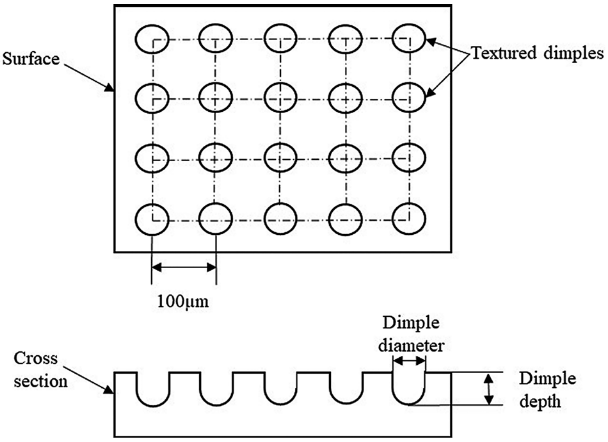

Fig. 2 Scheme of the texturing pattern

applying a laser wavelength of 532 nm and a power of 1 W. Scanning was repeated for 2000 shots per point to produce a dimple. Non-textured samples were used for comparison to measure the effectiveness of the textured samples.

2.3 Morphology and structural characterisation

The surface morphologies of the laser-textured coatings were observed by using a Keyence VHX-1000 digital microscope at 900 × magnification. Additionally, the morphology of the coatings with various surface roughness parameters was observed by a Park Systems NX-10 scanning probe microscope. Amongst the various surface roughness parameters, the arithmetic average surface roughness (*Ra*), root mean square surface roughness (*Rq*), skewness (*Rsk*) and kurtosis (*Rku*) were measured, and their possible relationships with the wettability of the laser-textured coating were investigated. *Ra* is the most commonly used surface roughness parameter; it is related to the water contact angle and thus surface repellence [15]. *Rsk* is a measure of the asymmetry of the surface profile. *Rku* is a measure of the peakedness or flatness of a surface. *Rsk* and *Rku* have both been used to predict the water mobility on a surface [15, 16]. For surface roughness measurements, three areas with size of 100 μm^2 on different parts of the samples were used.

2.4 Wetting characterisation

Static contact angle imaging and angle measurement of the laser-textured coatings were conducted using a sessile droplet method at room temperature and humidity. The static contact angle was measured by placing a 1 μl droplet of water on the surface of samples. The image was captured and analysed to calculate the contact angle. A DMe-201 high-speed camera (Kyowa Interface Science Co. Ltd) was used for the contact angle measurement. Image analysis and measurements were performed using the FAMAS software. The measurements were repeated three times on three different samples with the same coating parameters.

3 Results and discussion

3.1 Morphology and structural characterisation

Top view surface profile micrographs of laser-textured plasma-sprayed TiO_2/ZnO coatings are shown in Fig. 3. Given the high in-flight particle temperature during the plasma spraying process, the coating was formed mostly from fully molten particles; semi-molten particles and large splats were visible on the top surface of the coatings. The profile images revealed that melted and unmelted particles were combined with the pores and cracks (Figs. 3(a)–(c)). The laser impact sites surrounding the dimples underwent material transformation. Ejected matter associated with the coating material can be observed around the dimples' vicinity. The material temperature is expected to increase during the laser–material interaction until melting and ejection occur on the surface as a result of a pressure drop [17]. The laser texturing process produced dimples with uniform diameters under the given operating parameters regardless of the coating compositions. The structured dimples had increased the surface contact area of the coating. By increasing the contact area of a solid surface, it exposes many of its particles to attack. Consequently, this effect increased the chance of collisions between particles

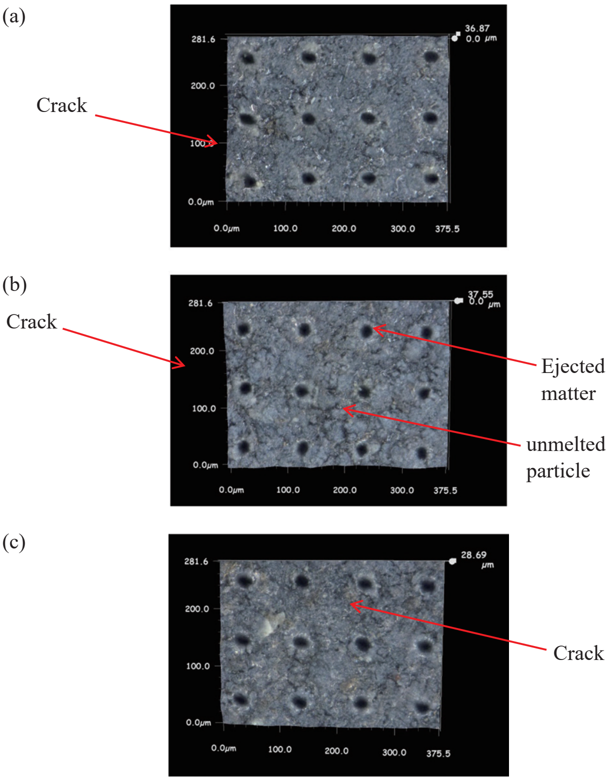

Fig. 3 Surface profile micrographs of the laser textured surface coating with composition of (a) 100% TiO_2 (b) 90% TiO_2 + 10% ZnO and (c) 70% TiO_2 + 30% ZnO

and reaction rates [18]. Therefore, modification of surface texture and chemical composition has considerable potential application in controlling wettability behavior. As mentioned in the Wenzel and Cassie–Baxter models, the surface texture and surface chemistry are the primary factors to determine liquid droplet behaviour on a solid surface, and texturing a surface with micro- or nanoscale architecture is essential to enhance hydrophobicity and hydrophilicity [19–21].

3.2 Wetting and roughness profile

The measured values of contact angle, *Ra*, *Rq*, *Rsk* and *Rku* for the six samples of laser-textured and non-textured plasma-sprayed TiO_2/ZnO coatings are presented in Table 3. As shown in the table, coatings exhibit relatively low contact angle, indicating an increased water absorbency especially for coatings with laser-textured surface. However, the non-textured coating for samples with 90% TiO_2 + 10% ZnO and 70% TiO_2 + 30% ZnO compositions exhibited a water contact angle above 90°, which is the minimum requirement for hydrophobic surfaces. On the other hand, all laser-textured surface coatings had a water contact angle less than 90°, which indicates a hydrophilic surface. Furthermore, coatings with 100% TiO_2 (0% ZnO) composition showed lower contact angle compared to coating with 10% and 30% ZnO contents. In this case, non-textured 100% TiO_2 samples with contact angle of 58.5° presented a hydrophilic surface (Fig. 4(a)), and laser-textured 100% TiO_2 sample with extremely low contact angle of less than 5° exhibited a superhydrophilic surface (Fig. 4(b)). This finding is attributed to the fact that in the presence of moisture, TiO_2 adsorbs H_2O molecules, resulting in hydrophilic properties [22]. In the present study, the laser-textured surface increased the surface area of TiO_2 coating exposed to moisture, endowing the surface with superhydrophilic properties. The mechanism of superhydrophilic surface properties of laser-textured TiO_2 coating is illustrated in Fig. 5. On the other hand, for the coating with the composition of ZnO exhibit hydrophobic surface properties as of the ZnO is an organic compound that is insoluble with water [23]. The ZnO content has led the coating surface to be water resist. This can be observed for the coating with 10% ZnO and 30% ZnO compositions exhibited a water contact angle above 90° for non- textured and above 50° for laser-textured surface.

Furthermore, the *Ra* and *Rq* values of laser-textured and non-textured TiO_2/ZnO coatings had slight differences (Table 3). This finding indicated that the surface roughness of the coating was not affected by the laser surface texturing process, and changes only occurred on the surface topographical properties of the coatings and considerably smooth surfaces due to the low values of *Ra* and *Rq*. In terms of *Rsk*, both laser-textured and non-textured TiO_2/ZnO coatings have positive values. Zero *Rsk* signifies perfect symmetry with the mean line, and positive *Rsk* values indicate that the surfaces of both types of coatings have a disproportionate number of high peaks [15]. An *Rku* value of 3 indicates normal distribution of peak and valleys throughout the sample surface. According to Table 3, non-textured and laser-textured TiO_2/ZnO coatings have *Rku* values significantly higher than 3, suggesting that these surfaces have comparatively more high peaks and deep valleys; *Rku* values less than 3 indicate the opposite [15]. No clear cut correlation between the surface roughness condition and water affinity and repellency properties were observed. Both of laser-textured and non-textured TiO_2/ZnO coatings shows low values of *Ra*

Table 3 Contact angle, arithmetic average surface roughness (*Ra*), root mean square surface roughness (*Rq*), skewness (*Rsk*) and kurtosis (*Rku*) for laser textured and non textured plasma sprayed TiO_2/ZnO coatings at various composition

Samples	Contact angle (θ)	*Ra* (μm)	*Rq* (μm)	*Rsk* (μm)	*Rku* (μm)
Laser textured 100% TiO_2	1.4 ± 2.42	0.49 ± 0.11	0.62 ± 0.09	0.36 ± 0.45	3.86 ± 2.36
Laser textured 90% TiO_2 + 10% ZnO	68.27 ± 5.6	0.36 ± 0.09	0.45 ± 0.07	0.23 ± 0.28	3.87 ± 1.73
Laser textured 70% TiO_2 + 30% ZnO	55.87 ± 17.11	0.56 ± 0.09	0.74 ± 0.12	0.17 ± 0.16	4.03 ± 0.41
Non textured 100% TiO_2	58.50 ± 3.5	0.46 ± 0.06	0.57 ± 0.09	0.23 ± 0.05	2.72 ± 0.29
Non textured 90% TiO_2 + 10% ZnO	98.83 ± 3.47	0.4 ± 0.08	0.52 ± 0.08	0.5 ± 0.11	4.02 ± 1.02
Non textured 70% TiO_2 + 30% ZnO	91.73 ± 17.2	0.42 ± 0.01	0.52 ± 0.01	0.37 ± 0.22	2.87 ± 0.42

(a) Non textured 100% TiO_2 (b) Laser textured 100%TiO_2

Fig. 4 Images of water duplet on (a) non textured 100% TiO_2 and (b) laser textured 100%TiO_2

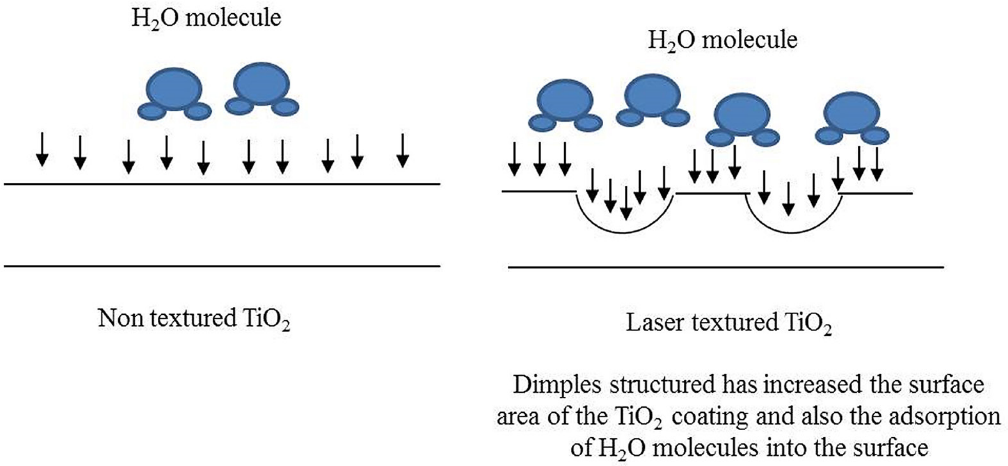

Fig. 5 Illustration for mechanism of superhydrophilic surface properties of laser textured TiO_2 coating

and *Rq* noticeably smooth surface but with different value of contact angle achieved that represented hydrophobic surface for non-textured coating and super hydrophilic surface for laser-textured coating. Besides, the positive *Rsk* value obtained for both laser-textured and non-textured TiO_2/ZnO coatings generating a different result in contact angle measurement for example for sample with laser- textured 100% TiO_2 showed superhydrophilic surface properties with *Rsk* value of 0.36 ± 0.45 while non-textured 70% TiO_2 + 30% ZnO exhibited hydrophilic properties with equivalent *Rsk* value of 0.37 ± 0.22. For this case, the coating composition (surface chemistry) plays important roles than the surface texture factor as of the coating was not affected by the laser surface texturing process.This finding is attributed to the fact that the surface chemistry is a determining factor when it comes to inherent wetting behaviour of ideally smooth surfaces [15].

4 Conclusions

Laser surface texturing is capable of producing submicron-size patterned coatings without altering its roughness properties. In short, the non-textured TiO_2/ZnO coatings indicated hydrophobic surface properties, whilst the laser-textured TiO_2/ZnO coatings exhibit hydrophilic surface features. The laser-textured with 100% TiO_2 displayed an extremely low contact angle (< 5°), indicating its superhydrophilicity in which the laser-textured surface had increased the surface area of TiO_2 coating, endowing the surface with superhydrophilic properties. However, no clear cut correlations between the surface roughness properties of non-textured and laser-textured TiO_2/ZnO coatings and the surface wettability properties were found, as the surface chemistry may became the determining factor in wetting behaviour on smooth surfaces.

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