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Corrosion Resistance of Micro-Textured Surface Modified Alumina-Titania Coating

J. A. Wahab[1], M. J. Ghazali[2] and M. N. Derman[1]

[1]Center of Excellence Geopolymer and Green Technology (CEGeoGTech), School of Materials Engineering, Universiti Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 2, Taman Muhibah, 02600 Jejawi, Arau, Perlis, Malaysia.
[2]Department of Mechanical and Materials Engineering, Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

Email: juyana@unimap.edu.my

Abstract. Effect of micro-texture on the corrosion resistance of alumina-titania coated mild steel was investigated. The micro-texture was fabricated on the coating surface via laser surface texturing technique. Tafel extrapolation and immersion test was conducted to measure the corrosion resistance and corrosion mechanism of the coating in 3.5% NaCl solution. The results indicated that the micro-texture contributes to a significant improvement of corrosion resistance due to the formation small volume of air trapped in the micro-grooves, which resist the penetration of corrosive ions and reduce the area of solid – liquid interface. The WCA indicated that the textured surface had low wettability. The SEM analysis showed the occurrence of uniform corrosion. The analysis of EDS revealed that there was formation of corrosion product at the coating-substrate interface. In short, the resistance towards corrosion was increased up to 73% indicating that the resistivity of the coating against corrosion was improved by engraving the micro-texture on its surface.

1. Introduction

Development of new materials has affected ceramic film and coating technology. The relatively high hardness and inertness of ceramic coating make this type of coating materials gain interest for protection of substrate materials against corrosion, oxidation and wear especially in marine environment. Oil and gas industry, shipping industry and the marine structures suffer from corrosion due to the exposure of aggressive ions in seawater. Combinations of wear, oxidation and corrosion problems contribute to failure factors that would eventually cause total shutdown, economic loss and hazardous effects [1]. Previous studies summarized that the corrosion problem is not fully solved only by applying a layer of coating on material surface. For these reasons, an improvement on corrosion protection method is needed to overcome these problems. A material with well-defined surface textures have been prepared in order to utilizes the beneficial effects of surface texturing technology. Generally, the main purpose of producing the texture is specifically to improve the roughness of substrate surface to micro- to nano-scale. The micro- or nano- scale textures on surface will affect the wettability characteristic (hydrophobicity) which can be described by two main models as proposed by Wenzel and Cassie and Baxter [2]. Such textured material which has low surface energy characteristic can be prepared either by depositing the coating material on a textured substrate [3] or directly structuring the surface by several technologies such as chemical etching [4], mechanical machining [5], lithography [6] and laser surface texturing [7].

In corrosion applications, plasma sprayed Al_2O_3 - 13%TiO_2 coating can reduce the corrosion rate due to its excellent properties; which are essential for corrosion applications [8]. The properties of Al_2O_3 - 13%TiO_2 coating, such as high hardness, low density, low thermal expansion and high resistance to oxidation and wear, make it widely used as a corrosion resistant coating, particularly in textile, machinery and printing industries [9, 10]. In marine environment, it has been a serious problem for many marine industrial structures such as hydraulic turbines, pumps and pipelines conveying solid particles [8]. Materials part or structures such the ships hulls, cooling-heat exchanger and structure in power plants are directly contact with corrosive ions (Cl-). They suffer from damaging effects induced by corrosion reaction and thus enhancing the material failures. The basic concept of corrosion protection by superhydrophobic surface is the micro-or nano-textured surface creates an interface layer with water by retaining air on the surface. The created interfaces that minimized the water molecules to contact the metal surface can prevent corrosive ion from adsorb and attack the surface materials.

The performance of Al_2O_3 - 13%TiO_2 coating, in these applications, could be made superior by applying some kind of texture on its surface. However, such experiments involving textured surfaces in mitigating corrosion problems have not been reported yet. In this study, the effect of micro-groove on the corrosion behaviour of plasma sprayed Al_2O_3 - 13%TiO_2 coating will be investigated. The micro-groove texture will be engraved on the Al_2O_3 - 13%TiO_2 surface using a short-pulsed laser system in a laser surface texturing process. Therefore, the performance of a laser textured Al_2O_3 - 13%TiO_2 coating in corrosion applications could be improved; thus enhancing the performance and lifespan of material components; especially in a harsh marine environment.

2. Experimental

2.1. Preparation of coating

To prepare the coating, commercial feedstock of Al_2O_3 - 13%TiO_2 (Metco 130SF), with a fine particle distribution, was deposited onto mild steel substrates using an atmospheric plasma spraying (APS) technique. The feedstock used had a fine particle distribution of -45+5 µm. A Praxair SG-100 plasma spray system, with a plasma torch mounted on a programmable robot was used in the deposition system. The surfaces of the substrates were sandblasted with alumina particles (mesh 24) as a pre-treatment to obtain good coating adhesion prior to the deposition process. A uniform coating thickness of 200–250 µm was prepared with a set of fixed spraying parameters of plasma power, 40 kW, primary gas pressure, 80 psi, secondary gas pressure, 60 psi, carrier gas pressure, 40 psi, powder feed rate, 3 rpm, and a stand-off distance of 100 mm.

2.2. Laser surface texturing

Table 1. Laser surface texturing parameters.

Parameter	Value
Model/system	Time Bandwidth, Duetto
Wavelength (nm)	1640
Pulse duration (ps)	10.3
Scanning speed	200 mm/s for 100 passes
Laser power (W)	2
Repetition rate (KHz)	300

A micro-groove texture was developed on the coating surface via a laser surface texturing technique. The Time Bandwidth, Duetto laser manufacturing system was used to produce the open-pore type texture, with a fixed distance of 150 µm and the depth of the groove was approximately 50 µm. A laser beam, with a diameter of approximately 5 mm, was introduced to the coating surface using a galvanometric scanner with a telecentric f-theta flat field lens. A galvanometer scanner was used to control the laser beam via a computer system. The features of the texture (Figure 1) were controlled via laser processing with a set of fixed parameters as shown in Table 1.

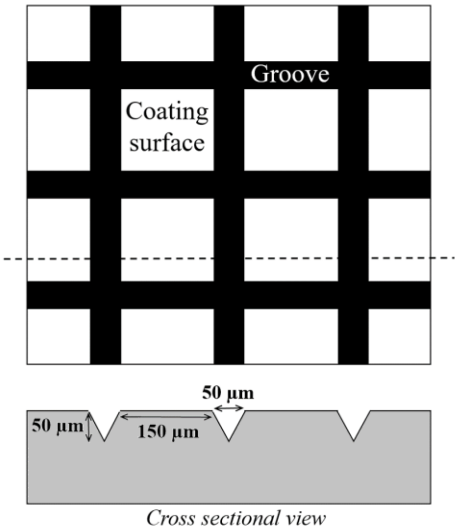

Figure 1. Schematic diagram of the texture feature with cross sectional view.

2.3. Characterisation and testing of the coating
The microstructural characteristics of the textured and non-textured coatings were observed using scanning electron microscope model FEI Nova NanoSEM 450. The phase compositions of the coatings were examined through X-ray diffraction (XRD) analysis, model Bruker D2 Phaser, Germany, using Cu-Kα radiation (1.5410Å).

2.4. Corrosion testing
The electrochemical properties of the coatings were studied using Tafel extrapolation method. The test was performed in a three-electrode cell with platinum rod as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode and a coating specimen as the working electrode. 3.5% NaCl solution was used as the electrolyte, which was maintain at room temperature. Corrosion testing system of Metrohm Autolab with Nova V1.1 software was used to determine the corrosion behaviour of the sample. The Tafel curve was generated by a scan rate of 0.5mV/s and a potential range of ±250 mV. The corrosion mechanism of the coating sample was evaluated by conducting immersion test in a solution of 3.5% NaCl with a constant pH value of 7. The pH of the NaCl solution was controlled by using NaOH and HCl solution. Before the immersion test, the uncoated area of the sample was mount by using epoxy resin to avoid contact with the solution. All the specimens were placed in a water bath at temperature of 27±3 °C. After 12 weeks of immersion test, the specimens were cleaned with ethanol in ultrasonic cleaner and then rinsed with distilled water. The SEM was used to analyse the morphology of the specimens cross sectional area. The EDX was used to examine the corrosion product element.

3. Results and discussion
3.1. Morphological examination
Figure 2 shows the surface morphology of both non-textured and textured coatings. From the image, it shows that laser processing has the capability to develop a groove texture at a micro size scale with high precision geometry on a ceramic coating surface. For the textured coating, no cracks or other damage formed on the surface after the laser surface texturing process.

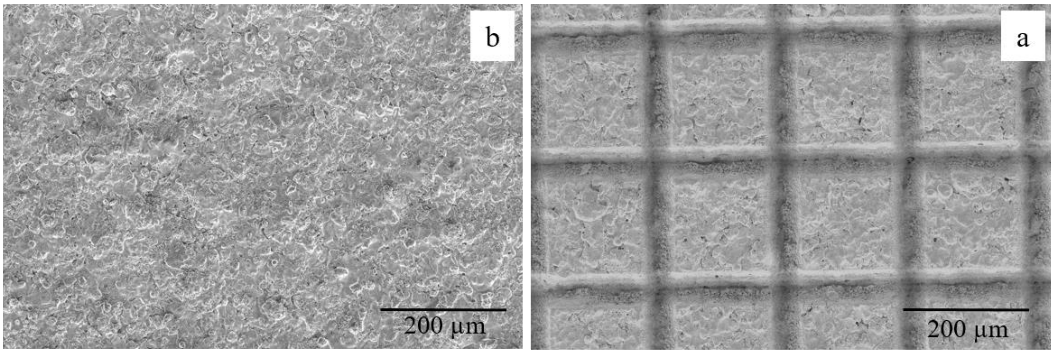

Figure 2. Surface morphology of the coating, a) non-textured and b) textured.

3.2. Corrosion behaviour

The effectiveness of grooves on coating surface in mitigating corrosion has been tested in this study by examine the electrochemical behaviour via Tafel extrapolation technique. The corrosion rate was determined by extracting the values of corrosion potential (E_{cor}) and corrosion current density (i_{cor}) from the Tafel plot. As can be seen in Figure 3, the corrosion potential of textured coating was more electropositive which was approaching a positive value. Meanwhile, for non-textured coating, the corrosion potential was more electronegative. The corrosion current density of non-textured coating also higher than that of textured coating, which indicated that the system of coating-substrate was less resistance to corrosion. It is important to mention that Al_2O_3 - 13%TiO_2 coating is an insulator, so that any current flowing in the coating system was due to the penetration of electrolyte through the coating. The non-textured coating exhibited a high corrosion resistance as compared to the non-textured coating. The calculated corrosion rate for both of textured and non-textured coating was around 1.63×10^{-3} mm/year and 6.06×10^{-3} mm/year, respectively. These results were found to be in agreement with Boinovich et al. [11] research, where they reported that the textured surface showed a reduction in the value of corrosion current density. Similar observation was discussed by the other researchers [12, 13], which stated that the reduction of corrosion current density value in the Tafel test was due to the changes in the wettability characteristic of the textured surface. The wettability characteristic of the surface can affect the corrosion performance of a material. Based on the investigation by Zhang and friends [14], the low wettability characteristic of the surface led to the high corrosion resistance properties. In their research, the superhydrophobic surface of steel contributed to large fraction of trapped air on surface, which was effectively prevents the direct contact between water droplet and the surface. Therefore, the corrosion reaction was decelerated and resulted in the reduction of corrosion rate of the steel.

Figure 4(a) and (b) displays the cross sectional area and EDS analysis of the coating after 12 weeks of immersion in NaCl solution. The cross sectional images of the corroded coatings revealed significant signs of degradation in the coating-substrate interface. The occurrence of uniform corrosion can be observed. The corrosion product formed at the coating-substrate interface indicated that corrosion reaction was occurred between the substrate and the NaCl solution. Further corrosion reaction at the coating-substrate interface will result in the delamination of the coating [15]. Based on the EDS analysis in Figure 4(c), the corrosion product consisted of Fe and O elements. This result showed that the corrosion product formed was attributed to the reaction between NaCl solution and the substrate. There was also Al element, which was originated from the coating compound.

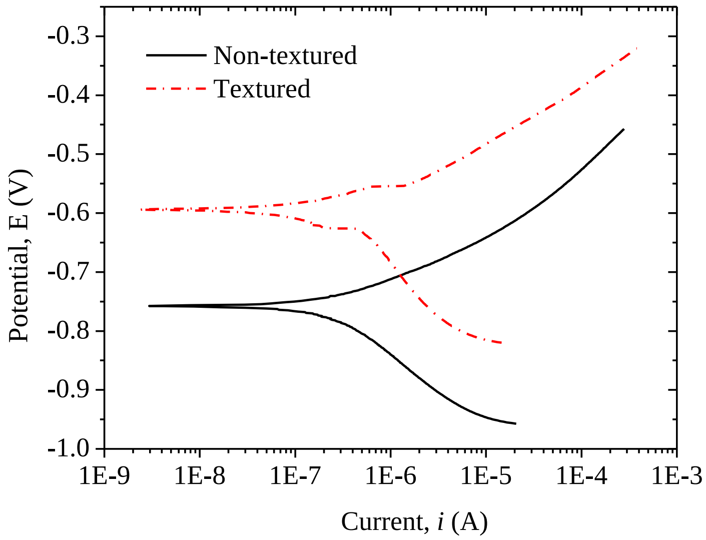

Figure 3. Tafel curve for the non-textured and textured coating.

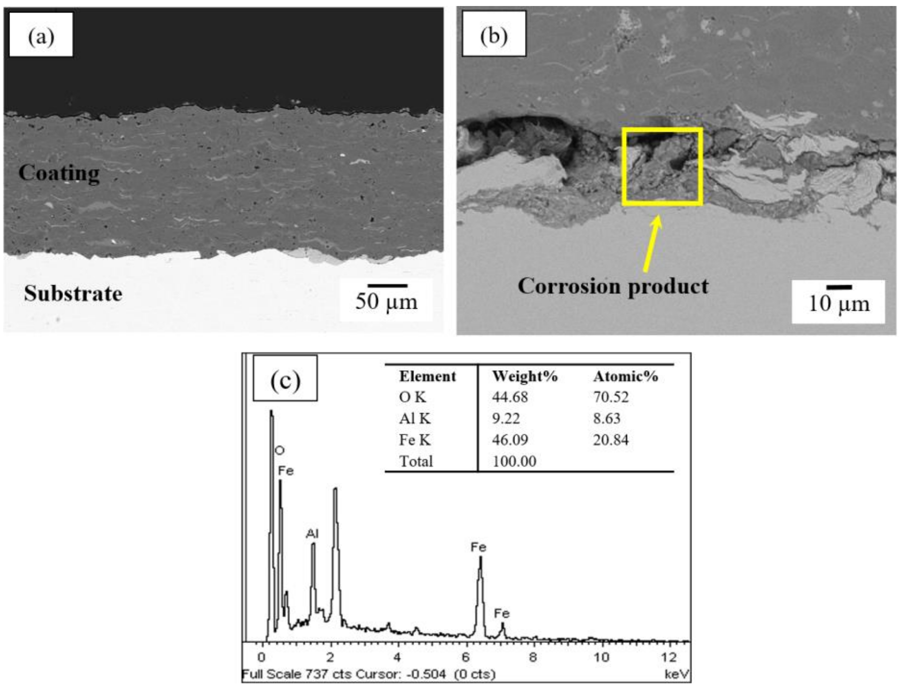

Figure 4. SEM image of cross sectional area of coating a) before immersion, b) after immersion and c) EDS analysis on corrosion product after immersion in 3.5% NaCl.

Based on the analysis of XRD pattern in Figure 5, there was corrosion product existed on the coating surface. The main corrosion product formed was consisted of iron oxide (Fe_2O_3) compound as confirmed by EDS. This result was supported by Tian and co-workers [16], which stated that the existence of Fe_2O_3 compound on the coating surface was due to the corrosion reaction that occurred at the interface of coating-substrate. Thus, it was confirmed that the coating layer consisted of porosity, which allowed the Fe_2O_3 compound moves out to reach at the coating surface.

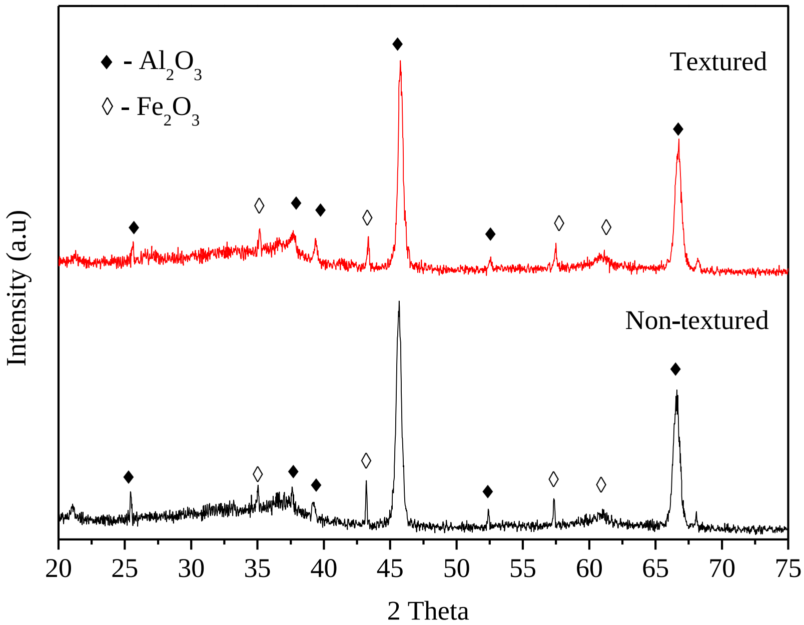

Figure 5. XRD pattern of non-textured and textured coatings after immersion in NaCl solution.

3.3. Corrosion mechanism

Through this study, it was clearly noted that introducing micro-grooves onto the surface enhanced the corrosion resistance of Al_2O_3 - 13%TiO_2 coating. From the results, it was showed the calculated corrosion rate revealed that the textured coating has high corrosion resistance as compared to that of non-textured coating. However, for both coating types, the electrolyte can penetrate through the coating layer and induce corrosion reaction at the interface of coating-substrate after 12 weeks of immersion in NaCl. This was occurred due to the existence of porosity in the coating system [15]. For the textured coating, the improvement in the corrosion resistance was due to the changes in wettability properties of the textured surface. As shown in Fig. 6, the contact angle of textured coating was around 97.1° ± 1.25 meanwhile for the non-textured coating, the contact angle was in the range of 74.5° ± 0.14. The surface of textured coating showed a hydrophobic characteristic, meanwhile the non-textured coating showed a hydrophilic characteristic. The hydrophobicity of the textured surface was resulted to the increment of the trapping air pockets in the grooves on textured coating surface. The trapped air pockets reduce the fractional area of electrolyte-coating interface and thus prevent direct contact of the NaCl solution with the coating surface [11], which led to the slow corrosion reaction. Therefore, the rate of corrosion reaction was reduced [14]. The investigation by Jagdheesh [17] revealed that the contact angle of alumina surface was increased around 153° ± 3 after laser surface texturing process. Similar trend was observed by [18], which stated that the laser surface texturing process was resulted to an increase in contact angle of zirconia surface up to 130°. The increment of surface contact angle (≥90°) value resulted to the high hydrophobicity characteristic of the surface [13]. High hydrophobicity of the surface has high capability to trap more air pockets on the surface [19], which can prevent the penetration of electrolytes into the substrate and thus, contributes to the higher corrosion resistance.

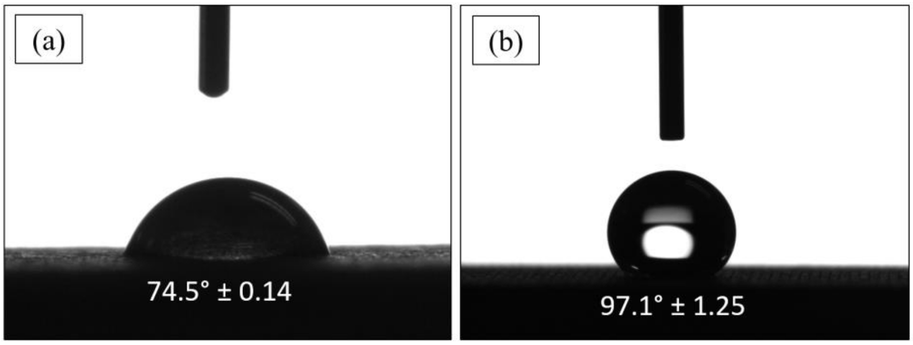

Figure 6. Contact angle of a) non-textured and b) textured coating.

4. Conclusion

Laser surface texturing is a convenient technique for developing surface texture on a ceramic coating with zero or minimal surface damage. In this study, a micro-groove texture, on the surface of plasma sprayed Al_2O_3 - 13%TiO_2 coating, was successfully fabricated via a laser surface texturing technique. The performance of the ceramic coating was found to be improved, particularly for tribological and corrosion applications. In the case of corrosion, the occurrence of uniform corrosion was detected and the resistance towards corrosion was increased up to 73%. Therefore, in this study, the resistivity of the coating against corrosion was improved by using the micro-groove texture on its surface. This would be extremely beneficial to several industries, particularly the marine industry.

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