SUPERHYDROPHOBIC AND ANTI-ICING COATINGS ON ALUMINIUM ALLOY SURFACES

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Abstract: A superhydrophobic and anti-icing surface was prepared by consecutive immersion in boiling water and sputtering of polytetrafluoroethylene on the surface of an aluminium alloy substrate. The immersion time in boiling water plays an important role on the surface morphology and water repellency of the deposited RF-sputtered Teflon coating. The Teflon-like coating deposited on a rough surface achieved with five-minute immersion in boiling water, provided a high static contact angle (~164 º) and low contact angle hysteresis (~4 º). Study of its wettability at low temperature showed that the superhydrophobic surface becomes rather hydrophobic at supercool temperatures. However, these results also showed a delayed freezing time of water droplets on its surface.

1. INTRODUCTION

Several methods have been reported in literature for the fabrication of superhydrophobic surfaces. However, most of these methods are substrate selective, involve complicated processes, raise environmental concerns or expensive instruments. So, developing an inexpensive approach to obtain industrially feasible superhydrophobic surfaces is important and necessary. In the present study, immersion in boiling water was used first to create a micro/nanostructured aluminium oxide underlayer on an alloy substrate [1]. In the second step, the resulting rough surface was coated with a RF-sputtered Teflon-like film.

2. RESULTS AND DISCUSSION

Immersion in boiling water is used in the creation of roughness at nanometric scale on the surface of aluminium alloys. The SEM images, displayed in Figs. 1a-1b, for aluminium alloys immersed for 3, and 10 minutes exhibit various structural features. Figure 1a shows a fine “flower-like” structure with a 20-150 nm petal size. A 10-minute treatment shows a “corn-flake” structure with cell wall thickness of about 10 nm and a 20- to 100-nm petal size (Fig. 1b). The study of surface roughness obtained by AFM analysis shows an increase of surface roughness at higher immersion time. The evolution of the static contact angle and hysteresis contact angle of Teflon-like coatings deposited on aluminium alloy surfaces as a function of immersion time is shown in Fig. 2. The results showed that by increasing the immersion time, the contact angle increased to 164±2º, whereas for immersions of more than 15 minutes, the contact angle decreased. The contact angle hysteresis decreased by increasing the immersion time to 3-5 minutes. However, immersion times above 5 minutes led to increased contact angle hysteresis. So, the high static water contact angle and the low contact angle hysteresis of a Teflon-like coating deposited on an aluminium surface immersed for 3-5 minutes indicate that Cassie and Baxter equation can explain its superhydrophobicity properties. Study of wettability at low temperature showed that superhydrophobic surfaces become rather hydrophobic at supercool temperatures. However, these results showed delayed freezing time of water droplets on the superhydrophobic surface.

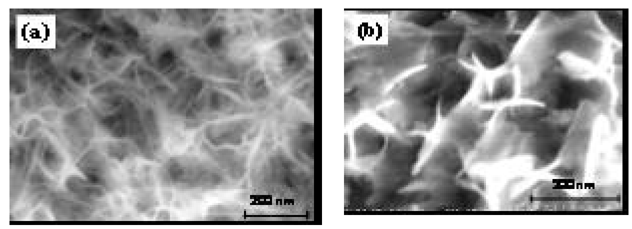

Figure 1: SEM image of the film produced on aluminium alloy immersed in boiling water for (a) 3 min (b) 10 min

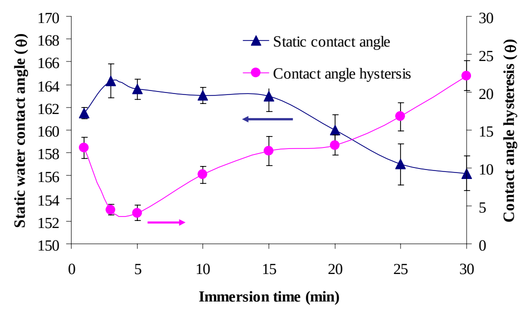

Figure 2: Variation of static contact angle and contact angle hysteresis of Teflon-like coatings deposited on treaded aluminium alloy in boiling water vs. time of immersion in water

3. CONCLUSION

Superhydrophobic surfaces were fabricated using two simple industrial processes. A Teflon-like coating deposited on a rough surface achieved with a five-minute immersion in boiling water, resulted in a high static contact angle (~164 º) and low contact angle hysteresis (~4 º). FTIR analysis showed the presence of CF_2 and CF_3 groups, responsible for the reduction of surface energy on the Teflon-like coating. Study of wettability at low temperature showed delayed freezing time of water droplets on the superhydrophobic surfaces.

4. REFERENCES

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***Abstract*— A superhydrophobic and anti-icing surface was prepared by consecutive immersion in boiling water and sputtering of polytetrafluoroethylene on the surface of an aluminium alloy substrate. The immersion time in boiling water plays an important role on the surface morphology and water repellency of the deposited RF-sputtered Teflon coating. The Teflon-like coating deposited on a rough surface achieved with five-minute immersion in boiling water, provided a high static contact angle (~164 º) and low contact angle hysteresis (~4 º). Study of its wettability at low temperature showed that the superhydrophobic surface becomes rather hydrophobic at supercool temperatures. However, these results also showed a delayed freezing time of water droplets on its surface.**

Keywords-component; *Superhydrophobic surface, aluminium alloy, anti-icing coating, Teflon*

I. INTRODUCTION

Superhydrophobic surfaces (surfaces with water contact angle higher than 150º) have attracted significant attention over the last two decades because of their water repellent, anti-icing, anti-sticking and self cleaning properties and also due to their potential for industrial applications [1-3]. However, it was found that the maximum contact angle that can be attained on a flat surface by lowering the surface energy cannot be greater than 120°. Superhydrophobic surfaces can be developed by a combination of surface micro- and nanostructures and low surface energy materials present on these surfaces.

Several methods have been reported in literature for the fabrication of superhydrophobic surfaces such as the sol-gel process, plasma treatment, electrochemical method, template method, vapour deposition, layer-by-layer method, and others [4-6]. These methods are mostly based on two approaches: (i) creation of a rough surface from low surface energy materials and (ii) creation of a rough surface followed by coating with a low surface energy material [7]. However, some of these methods are substrate selective, involve complicated process, raise environmental concern or expensive instruments. So, developing an inexpensive approach to obtain an industrially feasible superhydrophobic surface is important and necessary. In the present study, immersion in boiling water was used first to create a micro/nanostructured aluminium oxide underlayer on an alloy substrate [8]. This method is called boehmitage (formation of boehmite, $Al_2O_3.H_2O(s)$), and is used industrially to improve the corrosion properties of aluminium. A variety of low surface energy materials such as fluorocarbons and silicones precursors can be used to create superhydrophobic surfaces on rough surfaces. Polytetrafluoroethylene (PTFE or Teflon®) is one of the best materials for reducing ice adhesion strength due to its low electrical permittivity of ~ 2.1, low surface energy and chemical stability [9]. However, PTFE is very difficult to deposit as a thin film due to its limited solubility in solvents. Nano-emulsions of PTFE particles can be used for such a purpose [9]. However, this technique requires sintering temperatures above the PTFE melting point, which can limit its industrial applications. On the other hand, a variety of CVD and PVD techniques can be used to deposit PTFE. The sputtering technique is widely used in electrical and mechanical industries because it is simple, time saving, and environmentally friendly, and because the resulting coatings have a uniform structure and excellent adhesion properties to most substrates. So, in the second step, the rough surfaces (water treated) were coated with a RF-sputtered Teflon-like film.

II. EXPERIMENTAL SECTION

Polished 6061 aluminium alloy coupons from Rio Tinto Alcan were used as substrate. Prior to being treated in boiling water, the coupons were degreased using acetone, and then rinsed carefully with deionized water. The samples were then boiled in distillated water to roughen the surfaces. To achieve different roughness levels, the duration of boiling was varied. The RF plasma-sputtering process was carried out in an HICP-600SB PECVD system, manufactured by Plasmionique Inc. The distance between the target (Teflon) and the substrates (aluminium) was set at 30 cm. After being evacuated to a base pressure of 2.0×10^{-6} Torr, argon gases were admitted into the chamber. The flow rate of the sputtering gas was controlled by an MKS mass flow controller (MFC) and set at 50 standard cubic centimeters per minute (sccm). The aluminium surface was pre-cleaned and pre-activated in 50 W plasma argon for 5 min [10]. The sputter deposition process was carried out under 50 W RF power for 20 minutes at 20 mTorr.

Sample surface morphology was examined using a LEO field emission scanning electron microscope (FESEM) and an atomic force microscope (AFM) (Digital Nanoscope IIIa by Digital Instruments). Water contact angle measurements were carried out using a Kruss DSA 100 goniometer (water drop volume ~ 4 µL). The static contact angles were acquired by fitting the symmetric water drops using the Laplace–Young method, which is theoretically considered to be the most accurate because it takes into account the distorted drop shape due to liquid weight. In order to measure the contact angle hysteresis, which is the difference between the advancing and receding contact angles, a commonly used experimental procedure was followed [11]. The advancing and receding contact angles were measured by holding the water drop with a stationary needle in contact with the surface. The substrate was moved slowly in one direction using a micrometric screw.

III. Results and discussion

Immersion in boiling water is used in the creation of roughness at nanometric scale on the surface of aluminium alloys. The hydrated oxide film growth process in a temperature range of 50-100 ºC was defined in three stages, including an incubation period (1-2 sec.), a period of rapid growth, followed by a slow growth stage after the first few minutes of immersion. At these temperatures, bayerite crystals first appear at still longer times and their growth would constitute the final stage. The presence of a rough nanostructure on the aluminium surfaces was investigated using SEM and AFM analyses. The SEM images, displayed in Figs. 1a-1c, for aluminium alloys immersed for 3, 5 and 10 minutes, exhibit various structural features. Figure 1a shows a fine “flower-like” structure with a 20-150 nm petal size. By increasing the boiling water immersion time (Fig. 1b), the petal size became wider and cell-wall thickness increased. The 10-minute treatment shows a “corn-flake” structure with cell wall thickness of about 10 nm and a 20 to 100 nm petal size (Fig. 1c) [12-13].

The study of surface roughness obtained by AFM analysis shows a smooth surface with a roughness of around 2.2 nm for the polished aluminium alloy surface. However, the results show that the surface roughness is strongly depended on the immersion time, being 28-, 33- and 52-nm for boiling times of 3, 5 and 10 minutes, respectively. Indeed, the hydrated aluminium oxide film in boiling water was reported to have a porosity that increased with the immersion time [14]. The roughening process can be attributed to chemical erosion of the freshly polished aluminium alloy surface by water at high temperature [15]. After deposition of a PTFE coating on the boiled samples, the surface became smoother and surface roughness of the PTFE deposited on the boiled samples for 3 and 10 minutes decreased to 23 and 45 nm, respectively.

The FTIR spectra show the details of the functional groups present in the material. Fig. 2 shows the spectra of an aluminium alloy treated in boiling water for 5 min and a Teflon-like coating deposited on it. There is a broad peak at 3420 cm^{-1} with an unresolved shoulder at 3120 cm^{-1}. These peaks are attributed to the hydroxyl stretching mode. The peak seen at 1070 cm^{-1} is attributed to hydroxyl bending vibration [14]. Peaks appear at 1630 cm^{-1}, due to the bending mode of interstitial water, at 750 cm^{-1} and 620 cm^{-1}, due to Al-O stretching vibration. [16]. New peaks appeared on the FTIR spectra of the Teflon deposited on the aluminium alloy treated in boiling water for 5 min (upper spectrum). Peaks related to asymmetric C–F stretching (1150 cm^{-1}), and CF_2 symmetric stretch vibrations (1242 cm^{-1}) and a weak peak of CF_3 vibrations (991 cm^{-1}) [4] also appeared.

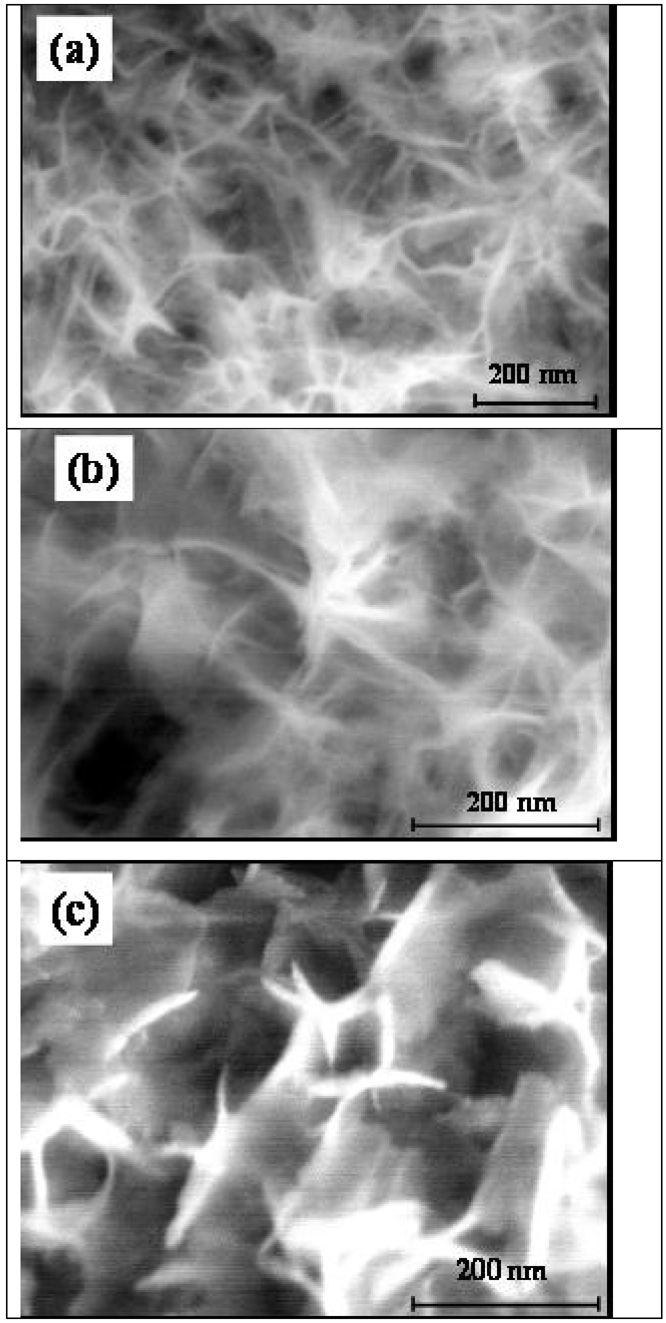

Figure 1. SEM image of the film produced on aluminium alloy immersed in boiling water for (a) 3 min (b) 5 min (c) 10 min

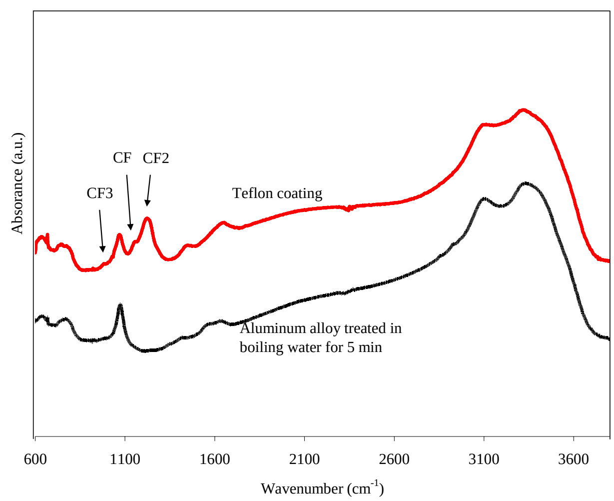

Figure 2. FTIR spectra from aluminium alloy immersed in boiling water for 5 min. The upper spectrum corresponds to the Teflon coating deposited on an aluminium alloy surface immersed in boiling water for 5 minutes

The evolution of the static contact angle and hysteresis contact angle of the Teflon-like coatings deposited on aluminium alloy surfaces as a function of immersion time is shown in Fig. 3. The static contact angle of a Teflon-like coating deposited on a polished aluminium alloy surface (without water treatment) is about 114±1º, while the Teflon-like coating on the aluminium alloy immersed in boiling water showed superhydrophobic behaviour. The water contact angle was about 161±3º for a 30-second immersion time. By increasing the immersion time, the contact angle increased to 164±2º, whereas for immersions of more than 15 minutes, the contact angle decreased. Measurement of the contact angle hysteresis (CAH) is very important to properly characterize a superhydrophobic surface [17]. For instance, a high contact angle water droplet deposited on a horizontal surface may remain pinned until the surface is tilted to a considerable angle. Therefore, the static contact angle alone is not enough to reflect the real wettability of a solid surface. Wenzel and Cassie-Baxter are the two main models that attempt describe the wetting of textured surfaces [18]. In Wenzel's model (homogenous interface), the liquid droplet retains contact at all points with the solid surface below it. Concerning the Cassie-Baxter model (composite interface), air pockets are trapped in the rough surface cavities, resulting in a composite solid–liquid–air interface, as opposed to the homogeneous solid–liquid interface. The contact angle hysteresis decreased by increasing the immersion time to 3-5 minutes. Immersion times above 5 minutes led to increased contact angle hysteresis. So, the high static water contact angle and the low contact angle hysteresis of the Teflon-like coating deposited on the immersed aluminium surface for 3-5 minutes indicate that the Cassie and Baxter equation can explain their superhydrophobicity properties. In fact, study of the films involving boiling water immersion showed that their structure depends on the immersion time. *Alwitt* explains that when aluminium is immersed in boiling water, the hydrated oxide film produced is pseudoboehmite with the composition Al_2O_3 $2.1H_2O$ [14]. So, the decrease in static contact angle and the increase in contact angle hysteresis could be explained by the increase in roughness and the variation in surface morphology during the second and third stages of film growth. Also, the needle-like structure observed for immersion times of 3-5 minutes could serve as a means of trapping sufficient air for low sliding angles to be exhibited.

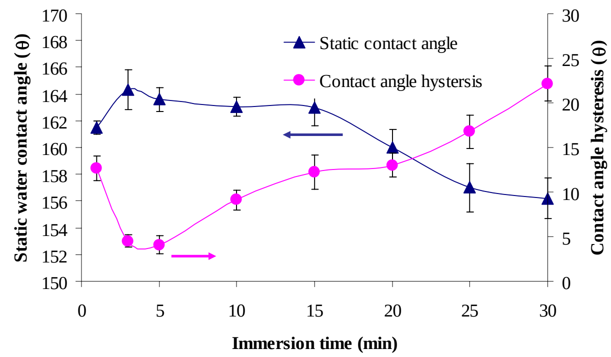

Figure 3. Variation of static contact angle and contact angle hysteresis of Teflon-like coatings deposited on treaded aluminium alloy in boiling water vs. time of immersion in water

The study of the wettability of superhydrophobic surfaces at supercooled temperature is of prime importance for the development of icephobic coatings [19, 20]. For this propose, the contact angle measurement of samples were carried out at low temperatures. For this purpose, the Kruss DSA 100 apparatus is fitted with a Peltier cooling element which allowed lowering the substrate temperature down to -30 ºC.

The wettability of the fabricated surfaces was evaluated in a wide range of temperature. Fig. 4 shows the variation of static contact of Teflon coatings deposited on water treated surface for 20 minutes (CAH ~ 14º) and 5 minutes (CAH ~ 4º) as a function of temperature. The results showed the superhydrophobic surface became rather hydrophobic with the surface temperature descending from 20 °C to -20 °C. However, the descent is more pronounced for superhydrophobic surfaces with higher CAH. When nanostructured surfaces are exposed to temperatures lower than zero, condensed water penetrates into the porosities of the coating and the water vapour condensation leads to a so-called Cassie-Wenzel regime transition resulting in lower contact angles [19]. This phenomenon seems be more important for the surface with higher CAH because of the higher water penetration in the rough surface cavities which can increase the surface contact with the supercooled surface.

Study of wettability at low temperature (-15 ºC) also showed delayed freezing time of water droplets on the superhydrophobic surface. In other words, the water droplets on a polished aluminium surface froze more quickly (about 5 sec.) than those on the superhydrophobic surface with low CAH (about 680 sec).

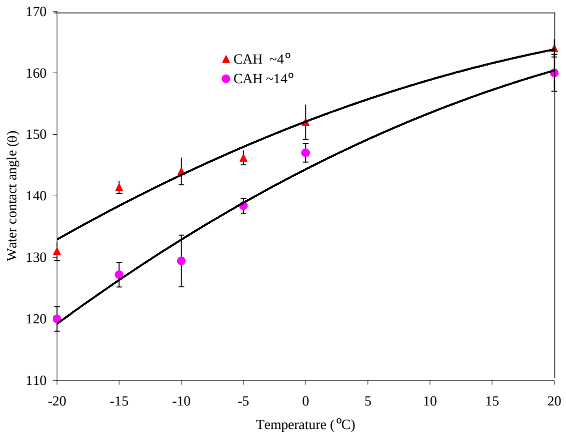

Figure 4. Evolution of static water contact angle of RF-sputtered Teflon coating deposited on water-treated aluminium alloy surface for 20 (CAH ~ 14º) and 5 (CAH ~4º) minutes versus temperature

IV. CONCLUSION

Superhydrophobic surfaces were fabricated using two simple industrial processes. Nanostructured patterns were created on aluminium alloy surfaces by immersion in boiling water. The rough surface was coated with RF-sputtered polytetrafluoroethylene. The immersion time in boiling water plays an important role on surface morphology and water repellency. A Teflon-like coating deposited on a rough surface achieved with a five-minute immersion in boiling water, resulted in a high static contact angle (~164 º) and low contact angle hysteresis (~4 º). FTIR analysis showed the presence of CF_2 and CF_3 groups, responsible for the reduction of surface energy on the Teflon-like coating. Study of wettability at low temperature showed that the superhydrophobic surface become rather hydrophobic with descending surface temperature from 20 °C to -20 °C. However, this reduction is more pronounced for superhydrophobic surfaces with higher CAH. These results also showed delayed freezing time of water droplets on the superhydrophobic surface as compared to those on a polished aluminium surface.

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