STABLE ICEPHOBIC TEFLON-LIKE COATINGS DEPOSITED ON AN ANODIZED ALUMINIUM SURFACE

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Abstract: In order to reduce ice accumulation on the surface of aluminium alloys, an icephobic and superhydrophobic coating was prepared by sputtering Teflon on an anodized aluminium surface. The superhydrophobic film showed an ice adhesion strength reduction of 3.5 times. However, these coatings showed a weak stability after several icing/de-icing cycles. In order to improve the cohesive strength of the Teflon-like coating, the input power of the discharge was increased during the sputtering process. XPS and contact angle analyses showed that an increase in input power renders the Teflon-like coating more stable. Low variations in ice adhesion strength were observed after as many as 9 icing/de-icing cycles.

1. INTRODUCTION

Superhydrophobic surfaces (water contact angle θ > 150º) have shown promising anti-icing performance. A superhydrophobic aluminium surface was produced by the deposition of a RF-sputtered Teflon-like coating on an anodized aluminium surface. The Teflon-like coatings exhibited a high static contact angle of ~ 165º with a very low contact angle hysteresis of ~ 3º [1]. Under atmospheric icing conditions, this superhydrophobic surface showed an ice-adhesion strength 3.5 times lower than a polished aluminium surface. However, as icephobic coatings require high stability and durability against several icing/de-icing cycles, the effect of sputtering power on the durability of the Teflon-like coating was tested after several icing/de-icing cycles.

2. RESULTS AND DISCUSSION

Study of the wettability of a Teflon-like coating deposited on anodized aluminium surfaces showed the importance of the anodization time and the sputtering time. The results showed, at the optimum conditions, that a RF-sputtered PTFE coating deposited on an anodized surface, exhibits a high static contact angle of ~ 165º with a very low contact angle hysteresis of ~ 3º. The icephobicity tests for this coating showed an ARF of 3.5 before any icing/de-icing cycle. However, its icephobic properties decreased after several icing/de-icing cycles. In order to improve the stability of the coating, input power was increased during the plasma-sputtering process. These results illustrate that a large amount of cross-linking in the Teflon-like coating deposited at high power (supported by the higher relative area of the C–C, C–CF peaks at 100 W) can improve the stability of Teflon-like coatings against several icing/de-icing cycles (Fig.1). The results of icephobicity tests for the Teflon-like coatings deposited at high power (100 W) showed a low variation of ARF due to a high degree of cross-linking improving the stability of the coating (Fig. 2).

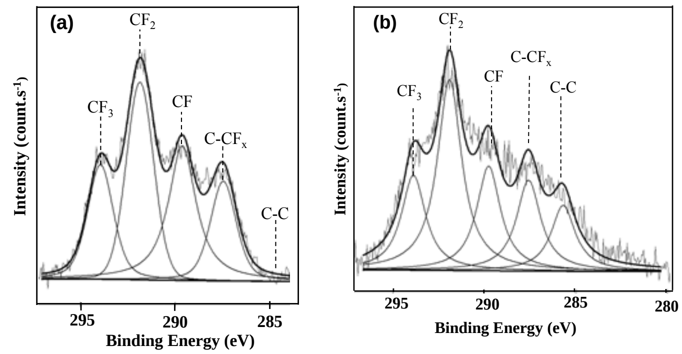

Figure 1: XPS C_{1s} spectra of Teflon-like coating deposited at high power (100w) on anodized aluminium surface (a) before icing/de-icing (b) after 6 icing/de-icing cycles

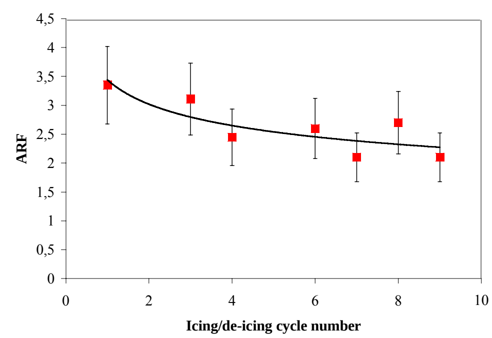

Figure 2: ARF value of Teflon-like coating deposited at 100 W as a function of the number of icing/de-icing tests

3. CONCLUSION

A superhydrophobic and icephobic surface on the surface of an aluminium alloy substrate was prepared using two inexpensive industrial processes (anodization and Teflon sputtering). Subjected to atmospheric icing conditions, this superhydrophobic film showed ice adhesion strength 3.5 times lower than on a polished aluminium surface. The effect of several operation parameters on the stability of the Teflon-like coating after several icing/de-icing cycles was studied. The results showed that at high power coating deposition, its cohesive strength was improved, with increased stability.

4. REFERENCES

[1] R. Jafari, R. Menini and M. Farzaneh, "Superhydrophobic and icephobic surfaces prepared by RF sputtered polytetrafluoroethylene coatings on anodized aluminium", Applied Surface Science, 257 (2010) pp. 1540–1543.

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***Abstract*— In order to reduce ice accumulation on the surface of aluminium alloys, an icephobic and superhydrophobic coating was prepared by sputtering polytetrafluoroethylene (PTFE or Teflon) on an anodized aluminium surface. The anodization was used to create a micro-nano structured aluminium oxide underlayer on the alloy substrate. The rough surface was coated with a RF-sputtered Teflon-like film. The Teflon-like coatings exhibited a high static contact angle of ~ 165º with a very low contact angle hysteresis of ~ 3º. The superhydrophobic film showed an ice adhesion strength reduction of 3.5 times. However, these coatings showed a decrease in stability after several icing/de-icing cycles. In order to improve theirdurability of the Teflon-like coating, the input power of the discharge was increased during the sputtering process. XPS and contact angle analyses showed that an increase in input power renders the Teflon-like coating more stable. Low variations in ice adhesion strength were observed after as many as 9 icing/de-icing cycles.**

Keywords:* *Superhydrophobic, Icephobic surface, Anodization, Alumium

I. Introduction

Ice accumulation can cause major problems on exposed structures, for instance on power, transportation and telecommunication networks, as was the case for Eastern Canada (1998) and in South China (2008) ice storms. Icephobic coatings appear to be an interesting solution to prevent ice accumulation [1]. While no coating is perfectly icephobic, some have been developed from which ice shedding requires very little energy [2-3]. Superhydrophobic surfaces (water contact angle > 150º) have shown promising anti-icing performance [4]. It has been shown that the maximum contact angle that can be attained on a flat surface by lowering the surface energy does not exceed 120° [3]. Moreover, the addition of roughness onto the surface can increase the contact angle of water without changing surface chemistry. So, superhydrophobic surfaces can be developed by a combination of low surface energy materials and surface micro and nanostructures [5-7].

For this study, a superhydrophobic aluminium surface was elaborated by the deposition of a RF-sputtered Teflon-like coating on an Al_2O_3 underlayer produced by anodization of an aluminium surface in a phosphoric acid electrolyte, resulting in a high static contact angle of ~ 165º and a very low contact angle hysteresis of ~ 3º [8]. Under atmospheric icing conditions, this superhydrophobic surface showed an ice adhesion strength 3.5 times lower than that on a polished aluminium surface. Indeed, icephobic coating applications require high surface stability and durability through several icing/de-icing cycles. The effect of sputtering power on the performance this Teflon-like coating after several icing/de-icing cycles was investigated.

II. Experimental section

Polished 6061 aluminium alloy coupons (2.54 cm × 2.54 cm × 0.15 cm) from Rio Tinto Alcan: Mg 1.0, Si 0.6, Cu 0.28, Cr 0.05, Zn 0.1, Fe 0.25 and Mn 0.15 (all in wt %) were used as the substrate. Prior to anodizing, the coupons were degreased using acetone, and then rinsed carefully with deionized water. The anodizing process was carried out in 10 % w/w solution of H3PO4 at T = 18 ºC at 50 V during 90 min. The RF plasma sputtering process was carried out in a 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 centimetres per minute (sccm). The aluminium surface was pre-cleaned and pre-activated in 50 W plasma argon for 5 min [9]. 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). Contact angle hysteresis was measured using a common experimental procedure [8].

The surface chemical composition was examined using X-ray photoelectron spectroscopy (XPS) at three different spots for each sample (PHI 5600-ci spectrometer, Physical Electronics). Survey and high-resolution spectra were acquired at a detection angle of 45° with respect to the normal of the surface, using the Kα line of standard aluminum (Kα = 1486.6 eV) and magnesium (Kα = 1253.6 eV) X-ray sources, respectively. For high resolution analyses, the Mg anode was used to provide better resolution and improved chemical shift characterization and attribution.

Ice adhesion strength measurements were made using the homemade centrifuge apparatus. Samples were attached at one end of aluminium beams and glaze ice (up to ~ 1 cm thickness) was accumulated in a refrigerated wind tunnel ($v = 10\ m.s^{-1}$, $T = -10$ ºC, water feed rate of 2.5 $g.m^{-3}$ and average droplet size of ~ 80 μm). This ice geometry was enough to avoid cohesion failure and provide reproducible de-icing results. The beam was spun at increasing rotational speed (T = -10 ºC) until ice detachment. As ice adhesion strength is assumed to be equal to the centrifugal force, $F = mr\omega2$, where m is the ice mass, r is the beam radius and ω is the rotation speed ($rad.s^{-1}$), the shear stress is then calculated as $\tau = F/A$, where A is the iced surface area. To reduce the bias caused by potential experimental errors, the adhesion reduction factors (ARF) were computed. ARF is the ratio between ice shear stresses of the bare polished aluminium and the coatings: ARF =τ(polished aluminium)/τ(coating).

III. Results and discussion

The SEM image of an anodized aluminium surface is typical of such phosphoric acid processes leading to large nanopores having thin walls, as shown in Fig.1a, which reveals the presence of some nanopores with a diameter of about 100 nm surrounded by a bird's nest structure. Figure 1b shows the anodized surface covered by the RF-sputtered PTFE thin film. Comparing both figures shows that the depth and diameter of the nanopores decreased slightly after PTFE thin film deposition. However, the nanopores are still present after PTFE deposition.

The study of wettability of the Teflon-like coating deposited on anodized aluminium surfaces showed the important effect of anodization time and the sputtering time. The results showed that, at optimum conditions, the RF-sputtered PTFE coating deposited on anodized surface, exhibited a high static contact angle of ~ 165º with a very low contact angle hysteresis of ~ 3º [8]. Also, under icing conditions, this superhydrophobic coating showed ice-adhesion strength 3.5 times lower than on a polished aluminium surface. In order to study of the stability of these coatings after several icing/de-icing cycles, water contact angles were measured for the Teflon-like coating deposited on anodized aluminium surfaces before and after several icing/de-icing cycles (Table 1). Without any ice-accumulation, the Teflon-like coating showed a high static contact angle of ~ 165º with a very low contact angle hysteresis of ~ 3º. After 3 icing/de-icing cycles, the coating seems to loose some of its hydrophobicity, since the static water contact angle decreases to ~ 150º and water contact angle hysteresis (CAH) reaches ~ 20º. After 6 icing/de-icing cycles, the coating lose its superhydrophobicity with a static contact angle of ~ 143º) and a very high CAH value of ~ 80º).

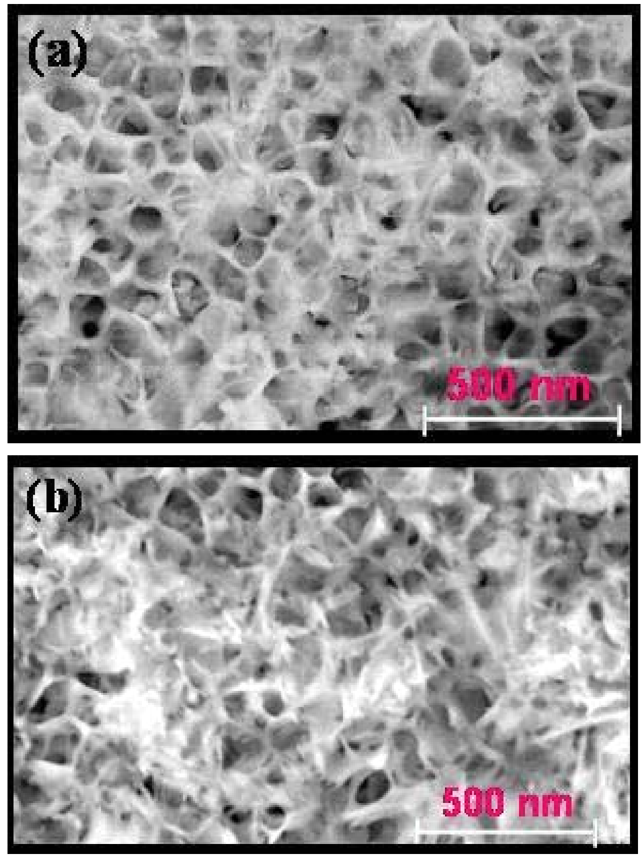

Figure 1. SEM image of (a) anodized aluminium and (b) RF-sputtered PTFE coating deposited on an anodized aluminium surface

TABLE I. Static contact angle and contact angle hysteresis values of Teflon-like coatings as a function of icing/de-icing cycles

Icing/de-icing Cycle number	Static water contact angle (θ)	Contact angle Hysteresis (θ)	
0	165	3	
3	150	20	
6	143	82	

Fig. 2 displays the results of icephobicity tests for the RF-sputtered PTFE coating after different icing/de-icing cycles. The ARF value of Teflon-like coating before any icing/de-icing, is about 3.5. However, after 3 icing/de-icing cycles ARF started to decrease. Moreover, a sharp decrease was observed after 4 cycles, with an ARF value of about 1. These results showed that the icephobic properties of the Teflon-like coating decrease after several icing/de-icing cycles which is compatible with the contact angle results.

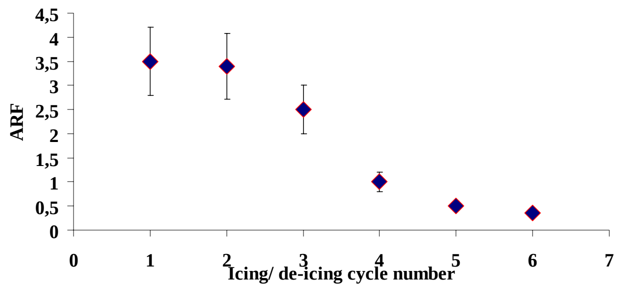

Figure 2. Variation of ice adhesion reduction factors (ARF) of Teflon-like coating deposited on anodized aluminium surface versus several icing/de-icing cycles number

For a better understanding of this phenomenon, the Teflon-like coatings were analyzed by XPS. The spectrum for the C_{1s} core level of a Teflon-like coating can be satisfactorily fitted by a combination of five distinct peaks: the peak at 285.1 eV corresponding to C-C moieties, the peak at 287.5 eV corresponding to $C\text{-}F_X$ species (hydrocarbon adjacent to a fluorocarbon group with x = 1 to 3), the peak at 289.6 eV corresponding to CF groups, the peak at 291.8 eV corresponding to CF_2 and the peak at 293.9 eV being due to CF_3 groups [10, 11]. The binding energy assignments and the relative peak area of each component are shown in Table 2. All the values are averaged on 3 different spots. It is well known that the presence of fluorine groups on the surface can lower the surface energy [12]. Zisman et al. reported that the surface free energy decreased in the following order: $-CH_2 > -CH_3 > -CF_2 > -CF_3$ [13]. Table 2 clearly shows the presence of high amounts of $-CF_3$ and $-CF_2$ groups on the Teflon-like coating before any icing/de-icing. After 6 icing/de-icing cycles, a high reduction of the fluorine groups on the surface (F/C decrease to 1.5) was observed. Also, the concentration of $-CF_3$ and $-CF_2$ groups, responsible of hydrophobic character of Teflon-like coating, was found to have significantly decreased.

TABLE II. THE PROPORTION OF C-C, C-CFX, CF, CF2, CF3 GROUPS AND F/C RATIO IN C1S SPECTROSCOPY OF TEFLON-LIKE COATINGS DEPOSITED AT 50 W

Assignment	C-C	$C\text{-}CF_X$	CF	CF_2	CF_3	F/C
Energy (eV)	285.1	287.5	289.6	291.8	293.9	—
Before icing/de-icing	1.4	16.2	19.8	43.9	18.7	2
After 6 icing/de-icing	22.2	19.9	17	27.4	13.2	1.5

In order to improve the cohesive strength of the coating, we increased the input power during the plasma-sputtering process. The XPS analyses of the Teflon-like coatings deposited at high power, showed that the F/C ratio decrease from 2, on samples prepared at 50 W, to 1.8, on those deposited at 100W. After 6 icing/de-icing cycles, no variation in the quantity of the fluorine groups on the surface of Teflon-like coatings deposited at high power was observed (F/C ~1.8).

These results illustrate that the large amount of cross-linking present in the Teflon-like coating deposited at high power (supported by the higher relative area of the C–C, C–CF peaks at 100 W, as shown in Fig. 3) can improve the stability of such coatings against several icing/de-icing cycles [14]. Increasing RF power results in a strong sputtering effect on the PTFE target and generates more ions and atoms in the charging space, thereby leading to a high level of cross-linking coating [15, 16].

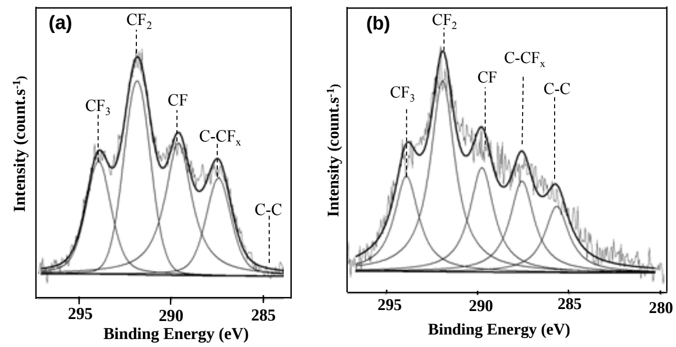

Figure 3. XPS C1s spectra of Teflon-like coating deposited at high power (100w) on anodized aluminium surface (a) before icing/de-icing (b) after 6 icing/de-icing cycles

Fig 4. displays the results of icephobicity tests for the Teflon-like coating deposited at high power (100 W). The ARF value of RF-sputtered PTFE coating at high power is about 3.4 before any icing/de-icing. After several icing/de-icing, a low variation of ARF can be observed. The ARF value reaches to about 2.5 after 9 icing/de-icing cycles due to gradually degrading ice releasing properties over repetitive icing/deicing. However, these results show an improvement in the stability of the Teflon-like coating deposited at high power due to a high degree of cross-linking.

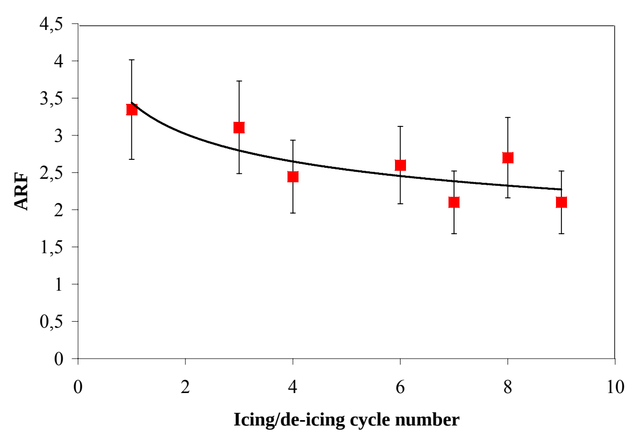

Figure 4. ARF value of Teflon-like coating deposited at 100 W as a function of the number of icing/deicing cycles.

IV. Conclusion

A superhydrophobic and icephobic surface on the surface of an aluminium alloy substrate, was prepared using two inexpensive industrial processes (anodization of the surface in phosphoric acid and sputtering of the anodized surface by polytetrafluoroethylene (PTFE or Teflon®)). The RF-sputtered PTFE coating deposited on the anodized surface exhibited a high static contact angle of ~ 165º with a very low contact angle hysteresis of ~ 3º. A high concentration of CF_3 and CF_2 groups, which are responsible for the hydrophobic behaviour of the coating, was revealed by X-ray photoelectron spectroscopy (XPS) analysis. Also, under icing conditions, this superhydrophobic film showed ice adhesion strength 3.5 times lower than on a polished aluminium surface. The effect of several operation parameters on the stability of the Teflon-like coating after several icing/de-icing cycles were investigated. The results showed that at high power coating deposition, its cohesive strength was improved, with increased stability.

Acknowledgment

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References

[1] M. Farzaneh, Atmospheric Icing of Power Networks, Springer, Berlin, 2008, p.381.

[2] V.F. Petrenko, S. Peng, "Reduction of ice adhesion to metal by using self-assembling monolayers (SAMs)", Can. J. Phys. 81 (2003) 387-393.

[3] D.K Sarkar, M. Farzaneh, "Superhydrophobic coatings with reduced ice adhesion", J. Adhes. Sci. Technol. 23 (2009) 1215-1237.

[4] S.A. Kulinich, M. Farzaneh, "Ice adhesion on super-hydrophobic surfaces", Appl. Surf. Sci. 255 (2009) 8153-8157.

[5] Z. Guo, W. Liu, B.L. Su, "Superhydrophobic surfaces: From natural to biomimetic to functional", Journal of Colloid and Interface Science 353 (2011) 335–355.

[6] M. Nosonovsky a, B. Bhushan, "Superhydrophobic surfaces and emerging applications: Non-adhesion, energy,green engineering", Current Opinion in Colloid & Interface Science 14 (2009) 270–280.

[7] R. Jafari and M. Farzaneh, "Fabrication of Superhydrophobic Nanostructured Surface on Aluminum Alloy", Applied Physics A, 102 (2011) pp. 195–199.

[8] R. Jafari, R. Menini and M. Farzaneh, "Superhydrophobic and icephobic surfaces prepared by RF sputtered polytetrafluoroethylene coatings on anodized aluminium", Applied Surface Science, 257 (2010) pp. 1540–1543

[9] R. Jafari, M. Tatoulian, W. Morscheidt, F. Arefi-Khonsari, " Stable plasma polymerized acrylic acid coating deposited on polyethylene (PE) films in a low frequency discharge (70 kHz)" Reactive & Functional Polymers 12 (2006) 1757-1765.

[10] P. Gonon, "Effect of nitrogen addition on the properties of C:F thin films deposited by RF sputtering", Eur. Phys. J. Appl. Phys. 32 (2005) 15-21.

[11] V. Stelmashuk, H. Biederman, D. Slavinska, J. Zemek, M. Trchova, "Plasma polymer films rf sputtered from PTFE under various argon pressures", Vacuum 77 (2005) 131-137.

[12] E. Burkarter, C.K. Saul, F. Thomazi, N.C. Cruz, L.S. Roman, W.H. Schreiner, "Superhydrophobic electrosprayed PTFE", Surf. Coat. Technol. 202 (2007) 194-198.

[13] E.F. Hare, E.G. Shafrin, W.A. Zisman, "Properties of films of adsorbed fluorinated acids", J. Phys. Chem. 58 (1954) 236-239.

[14] Z. Ning, S. Cheng, L. Chen, "Effects of deposition temperature on the structure and thermal stability of a-C:F films with low dielectric constant", Materials Science in Semiconductor Processing 8 (2005) 467–471.

[15] G. Tang, X. Ma, M. Sun, X. Li, "Mechanical characterization of ultra-thin fluorocarbon films deposited by R.F. magnetron sputtering", Carbon 43 (2005) 345–350.

[16] Y. Yamada and T. Kurobe, "X-Ray Photoelectron Spectroscopy of Fluorocarbon Films Deposited by RF Sputtering", Jpn. J. Appl. Phys., 32 (1993)32, 5090-5094

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