

WETTABILITY BEHAVIOR OF SUPERHYDROPHOBIC SILICONE RUBBER COATINGS AT SUPERCOOLED TEMPERATURES

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Abstract:

A superhydrophobic surface was prepared by anodization of aluminum substrates in phosphoric acid followed by RTV silicone rubber coating. Study of the surface wetting properties showed a high static contact angle, up to 160 ° for the treated surfaces at room temperature.

Scanning electron microscopy image analysis showed that bird's nest and beehive structures had formed on the anodized surfaces at 50 V and 80 V. The results showed that higher anodizing voltage leads to larger pore sizes.

The freezing behaviour of 4- μ L water droplets was investigated on nanostructured aluminum surfaces and compared with that on flat surfaces and hydrophobic aluminum surface.

1. INTRODUCTION

Protecting aluminum ground wires and phase conductors of overhead power lines against ice adhesion through application of superhydrophobic coatings with icephobic properties on their surfaces seems to be an interesting solution as compared to the current ones. Superhydrophobic surfaces can be prepared by the combination of a micro-nano surface structure and low surface energy materials. Anodic aluminum oxide has been proposed as a suitable industrial process to develop nano-structured films and to improve resistance to corrosion and wear.

In this study, a superhydrophobic surface was obtained by anodization of aluminum substrates in phosphoric acid followed by RTV silicone rubber coating. Study of the surface wetting properties showed a high static contact angle, up to 160 ° for the treated surfaces at room temperature.

2. RESULTS AND DISCUSSION

The effect of anodizing voltage on surface morphology was investigated as shown in Fig. 1. As anodizing voltage was increased, the surface pores became wider, indicating that the anodization voltage affects the size and form of the pores. The development of pore structure was found to be proportional to applied voltage which is consistent with what was reported in [1].

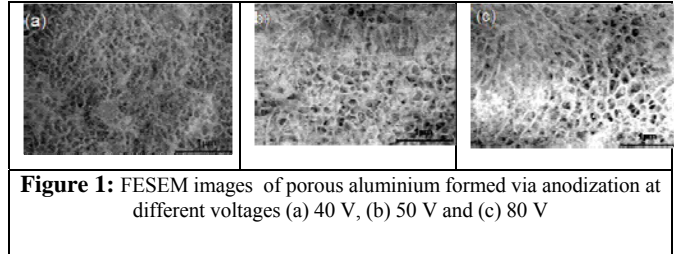


Figure 1: FESEM images of porous aluminium formed via anodization at different voltages (a) 40 V, (b) 50 V and (c) 80 V

Fig. 2 showed the variations in water contact angle of RTV silicone rubber coated on aluminium porous surfaces as a function of anodization voltage. Study of water contact angles showed the best wettability results were obtained at 50-V anodizing voltage. The water droplet freezing time for the superhydrophobic surface (50 V) was 4-5 min which is significantly longer than on the flat uncoated Al surface and the RTV-coated hand-polished surface (few

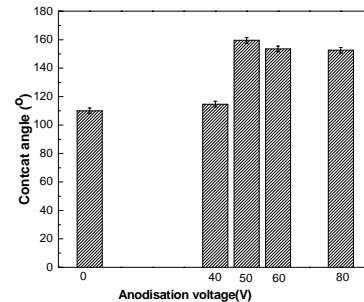


Figure 2: Contact angle of the as-prepared surfaces as a function of applied voltage

seconds).

3. CONCLUSION

The combination of surface anodizing and RTV silicone rubber coating resulted in significantly enhanced wettability of aluminium alloy 6061. The effect of anodization voltages on the morphology of the anodic oxide formed was evaluated. Freezing time was considerably delayed for the superhydrophobic surfaces compared to hydrophobic and Al bar surfaces.

4. REFERENCES

[1] J. Kim, M. K. Chaudhury, M.J. Oweny, Diffusion of Low Molecular Weight Siloxane from Bulk to Surface, J. Colloid. Interface. Sci. 226 (2000) 231-236.

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Abstract—A superhydrophobic surface was prepared by anodization of aluminum substrates in phosphoric acid followed by RTV silicone rubber coating. Study of the surface wetting properties showed a high static contact angle, up to 160° for the treated surfaces at room temperature.

Scanning electron microscopy image analysis showed that bird's nest and beehive structures had formed on the anodized surfaces at 50 V and 80 V. The results showed that higher anodizing voltage leads to larger pore sizes.

The freezing behaviour of 4- μ L water droplets was investigated on nanostructured aluminum surfaces and compared with that on flat surfaces and hydrophobic aluminum surface.

Keywords-component; anodizing voltage; silicone rubber ; superhydrophobic

I. INTRODUCTION

Ice and wet snow accumulation on power network equipment is a serious problem encountered in cold climate regions as demonstrated by the ice storms that hit Eastern Canada and Southern China in 1998 and 2008, respectively [1-3].

Recently, superhydrophobic surfaces with a water contact angle (CA) larger than 150° have gained considerable attention because of their various practical applications as coatings on exposed structures such as overhead transmission and distribution lines as well as their substation equipment. Moreover, superhydrophobic surfaces prepared by applying low surface energy materials on rough surfaces have shown promising anti-icing performance [4-8]. So, icephobic surfaces have attracted a great interest compared to de-icing fluid active methods to reduce ice or snow accumulation on high voltage overhead transmission lines.

Several methods have been used to create nano or micro structures on the aluminium surfaces such as etching in acid [9-11], alkali solution [12, 13] and anodizing in different solution [7,14].

In the present study, anodic aluminium oxidization has been proposed as a suitable industrial process that increases resistance to corrosion and wear. Moreover, this method leads to the formation of nanopore structured films [14, 15] which also reduce the ice surface contact with the substrate. The degree of ordering and the dimensions of the nanopores can be tuned by adjusting the anodizing conditions, such as the voltage, electrolyte type, duration, and temperature [16]. Moreover, the control of surface roughness is essential in preparing superhydrophobic surfaces.

Recently, the application of room temperature vulcanized (RTV) silicone rubber coatings has been investigated as an effective solution to develop a hydrophobic surfaces for external insulators. Such coatings help prevent continuous water filming on the surface and can be applied by several methods such as dipping, painting, or spraying [17]. Furthermore, silicone rubber exhibits the ability to restore its hydrophobicity even after a pollution layer has built up on the surface [17, 18]. This property has been attributed to the diffusion of low molecular weight (LMW) silicone fluid from the coating onto the polluted deposits [18].

In the present study, several anodization voltages were applied to create various nanostructured surfaces. Superhydrophobic surfaces were provided using RTV silicone rubber coating on the anodized samples. The wettability behaviour for the prepared coating was also evaluated.

I. EXPERIMENTAL PROCEDURE

Coupons of 6061 Al alloy supplied by 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 %) of dimension 2.54 cm×2.54 cm×0.15 cm used as substrate. The samples were hand-polished before being anodized. The counter electrode was a 5.08 x 7.62 cm 6061 Al alloy plate and the electrochemical reaction was carried out at constant voltage. The anodised aluminium surfaces were prepared by an electrochemical bath consisting of a 10 % w/w solution of H₃PO₄ at T = 18° C

during 90 min. Prior to the anodization process, the samples were degreased using an ultrasonic bath of acetone followed by deionised water, each for 5 minutes. The anodizing process was performed at the following anodizing voltages: 40 , 50 , 60 and 80 V.

RTV silicone rubber 3-4190 was purchased from Dow corning. This product was selected because it does not contain fillers. First, the RTV silicone rubber was diluted by adding hexane in a volume ratio of 1:12. Then, the solution was applied on the aluminium substrates using a sol-gel spin coating procedure (WS-400B-6NPP spin-coater from Laurel). The spinning speed was set at 3000 rpm (20 s) and 2500 rpm (15 s) for the first and second stages, respectively. Heat treatment of the coatings was done at 85° C in air overnight to remove residual solvents.

The surface morphology of the samples was evaluated using a LEO field emission scanning electron microscope (FESEM). Water contact angle measurements were carried out by a Kruss DSA 100 goniometer (water droplet volume ~ 4 µL). This apparatus was fitted with a Peltier cooling element which allowed lowering the substrate temperature down to -30 °C.

II. RESULTS AND DISCUSSION

The effect of anodizing voltage on surface morphology was investigated. SEM microphotographs taken for Al anodised samples with three applied voltage are shown in Fig. 1.

For anodization at 40 V, the surface of the oxide formed was characterized by an irregular structure with small pores. The resulting pores formed were non-uniform and discontinuous (Fig. 1a).

A hexagonal “bird’s nest” structure separated by thinner pore walls was observed on the pores formed at 50 V anodising voltage, as shown in Fig. 1b. At 80 V, the pores were continuously formed on the surface, becoming wider and deeper, with a “beehive structure” (see Fig. 1c).

As the anodizing voltage was increased, the pores became wider, indicating that the anodization voltage affects the size and form of the pores. The average pore diameter anodized with 40 , 50, and 80 V was around 50, 80, and 120 nm, respectively. The development of pore structure was found to be proportional to the applied voltage which is consistent with what was reported in [18, 19].

Contact angles are the result of the molecular interactions of solid-liquid, liquid-gas, and gas-liquid at the three-phase contact point. The sessile droplet method, which measures the contact angle (CA) of a water droplet on a surface, was used to characterize the wetting property of the surfaces. For that purpose, the samples were placed on a test stage and a water droplet was introduced onto the surface through a microsyringe. At least five different measurements were performed on different areas of each sample.

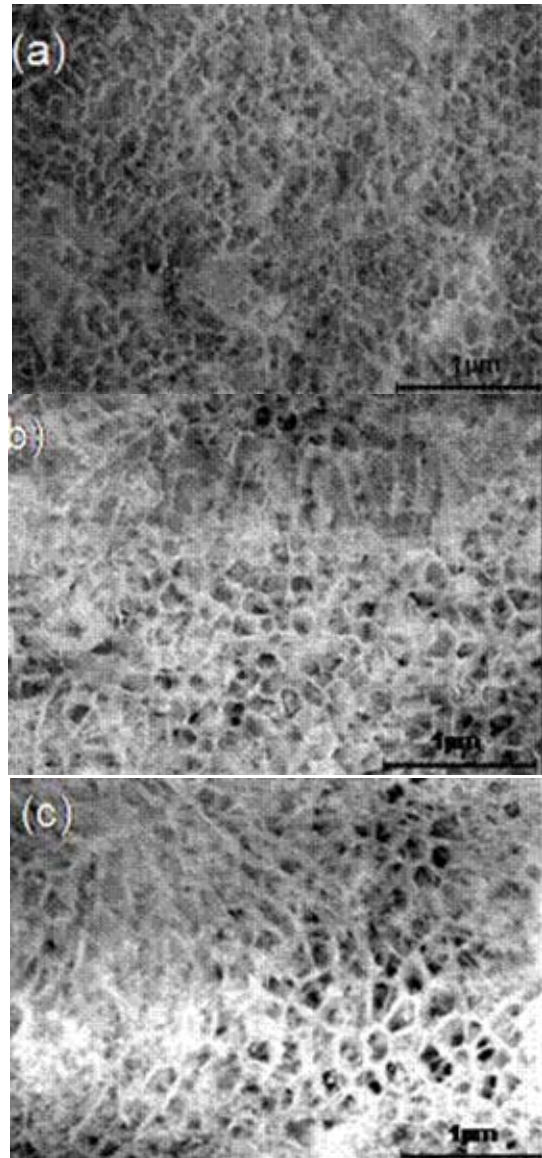


Figure 1. FESEM images of porous aluminium formed via anodisation at different voltages (a) 40 V, (b) 50 V and (c) 80 V.

Figure 2 shows the variations in water contact angle of RTV silicone rubber coated on aluminium porous surfaces as a function of anodization voltage.

The water contact angle of a hand-polished Al bar was $110^\circ \pm 2$. Application of 40-V anodising voltage resulted in a little increase of contact angle ($114^\circ \pm 2$).

Increasing voltage to 50 V led to a high contact angle and the surface became superhydrophobic. Applying RTV silicone rubber coating on more highly anodised surfaces (50 V and more) resulted in superhydrophobic behaviour whereas a 40-V anodised surface with the same coating remained hydrophobic.

However, increasing the voltage to more than 50 V resulted in a slight decrease of static contact angle.

The results showed that the best wettability was found in the

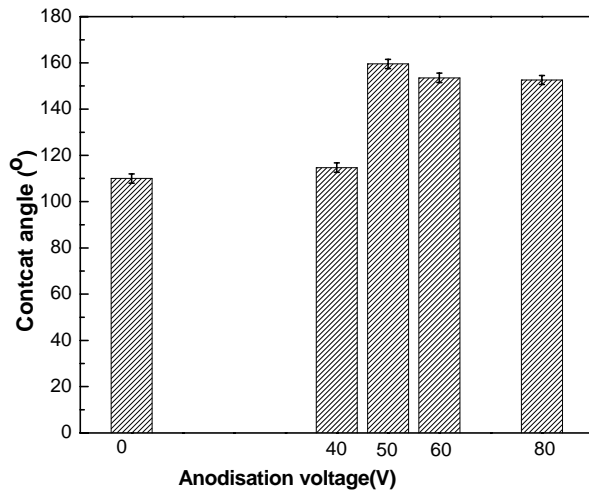


Figure 2. Contact angle of the as-prepared surfaces as a function of applied voltage

case of the nanostructured surface created by a 50-V anodising voltage. Otherwise, an appropriate combination of micro/nano structure (see Fig. 1b) was created at this voltage.

The study of the water contact angle at supercooled temperatures is of prime importance for the development of icephobic and superhydrophobic coatings [20, 21].

For this propose, contact angle measurements were carried out at temperature as low as -15°C . Each measurement was repeated three times. Figure 4 shows the freezing process of a water droplet ($4\ \mu\text{L}$) on a 50-V RTV superhydrophobic surface.

The water droplet freezing time for the flat uncoated Al surface and the RTV-coated hand-polished surface was short, and water froze just within a few seconds. However droplet crystallization on superhydrophobic surface (50V) was observed after 4-5 min.

Fig. 3 illustrates the water droplet freezing on a 50-V RV superhydrophobic surface. Indeed, after 205 s, the droplet shape begins to changing and become expanded, appearing ice nucleation at the solid-water interface. It was observed that the interface between water and ice kept moving from bottom to top during the transient heat conduction after which droplet crystallization occurred completely.

Indeed, entrapped air in the cavities of superhydrophobic

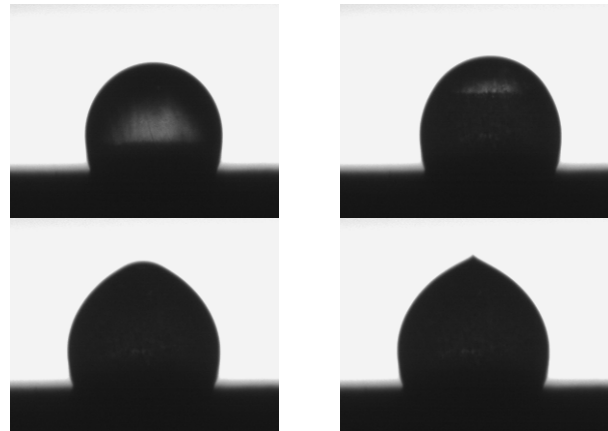


Figure 3. Image sequences of water droplets ($4\ \mu\text{L}$) freezing process on anodised Al at 50-V applied voltage under a constant temperature of -15°C .

surfaces could acts as a thermal barrier between the solid and the liquid delaying freezing time on these surfaces [21].

III. CONCLUSIONS

The combination of surface anodizing and RTV silicone rubber coating resulted in significantly enhanced wettability of aluminium alloy 6061. The effect of anodization voltages on the morphology of the anodic oxide formed was evaluated. The results showed that higher anodising voltages led to the larger pore diameters. The regularity of pore arrangement as well as the size of the pores increased with higher anodizing voltages. “Bird’s nest” and “beehive” structure was observed on the anodised surface of 50 V and 80 V. Study of water contact angles showed the best result of wettability for 50 V anodising voltage. Freezing time was considerably delayed for the superhydrophobic surfaces compared to hydrophobic and Al bar surfaces.

IV. ACKNOWLEDGMENT

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V. REFERENCES

- [1] F. Wang, C. Li, Yuzhen Lv, F. Lv, Y. Du, Ice accretion on superhydrophobic aluminum surfaces under low-temperature conditions, *Cold Regions Science and Technology* 62 (2010) 29-33.

- [2] Z.L. Jiang, J.Z. Lu, H.C. Lei, F.Y. Huang, Analysis of the causes of tower collapses in Hunan during the 2008 ice storm, *High Voltage Engineering* 34 (11) (2008) 2468–2474.
- [3] M. Farzaneh, *Atmospheric Icing of Power Networks*, Springer, Berlin, 2008, p.381.
- [4] S.A. Kulinich, M. Farzaneh, How Wetting Hysteresis Influences Ice Adhesion Strength on Superhydrophobic Surfaces, *Langmuir*, vol. 25 pp.8854-8856, August 2009.
- [5] S.A. Kulinich, M. Farzaneh, Ice adhesion on super-hydrophobic surfaces, *Appl. Surf. Sci.*, vol. 255, pp. 8153-8157, June 2009.
- [6] S.A. Kulinich, M. Farzaneh, «On ice-releasing properties of rough hydrophobic coatings». *Cold Regions Science and Technology*, vol. 65, no.11, pp.60-64, January 2011.
- [7] R. Menini, M. Farzaneh, Elaboration of Al₂O₃/PTFE icephobic coatings for protecting aluminum surfaces, *Surf. Coat. Technol.* vol. 203, pp. 1941–1946, February 2009.
- [8] Y. Liu, X. Chen, J.H. Xin, Super-hydrophobic surfaces from a simple coating method: a bionic nanoengineering Approach, *Nanotechnology*, vol. 17, pp. 3259-3263, July 2006.
- [10] Q. BT, S. ZQ, Fabrication of superhydrophobic surfaces by dislocation-selective chemical etching on aluminum, copper, and zinc substrates, *Langmuir*, vol. 21, pp. 9007–9009, August 2005.
- [11] Z.Chen, Y. Guo, S. Fang, A facial approach to fabricate superhydrophobic aluminum surface, *Surf. Interface Anal.* 42 (2010) 1-6.
- [12] Z. Guo, F. Zhou, J. Hao, W. Liu, Stable biomimetic super-hydrophobic engineering materials, *J Am. Chem. Soc.*, vol. 127, pp. 15670-15671, October 2005.
- [13] X. Fu, X. He, Fabrication of super-hydrophobic surfaces on aluminum alloy substrates, *Appl. Surf. Sci.*, vol. 255, pp. 1776-1781, December 2008.
- [14] R. Jafari, R. Menini and M. Farzaneh, Superhydrophobic and icephobic surfaces prepared by RF-sputtered polytetrafluoroethylene coatings, *Appl. Surf. Sci.*, vol. 257, pp. 1540-1543, November 2010.
- [15] J. Ye, Q. Yin, Y. Zhou, Superhydrophilicity of anodic aluminum oxide films: From “honeycomb” to “bird's nest”, *Thin Solid Films*, vol.517, pp. 6012-6015, September 2009.
- [16] G.D. Sulka, K.G. Parkola, Anodising potential influence on well-ordered nanostructures formed by anodisation of aluminum in sulphuric acids, *Thin solid films*, vol. 515, pp. 338-345, September 2006.
- [17] G. Momen, M. Farzaneh, Survey of micro/nano filler use to improve silicone rubber for outdoor insulators, *Reviews on advanced materials science*, under press.
- [18] J. Kim, M. K. Chaudhury, M.J. Oweny, Diffusion of Low Molecular Weight Siloxane from Bulk to Surface, *J. Colloid. Interface. Sci.* vol. 226 pp. 231-236, June 2000.
- [19] G.Q. Ding, R. Yang, J.N. Ding, N. Y. Yuan, Y.Y. Zhu, Fabrication of Porous Anodic Alumina with Ultrasmall Nanopores, *Nanoscale Res. Lett.* vol. 5, pp. 1257-1263, August 2010.
- [20] L. Yin, Q. Xia, J. Xue, S. Yang, Q. Wang, Q. Chen, In situ investigation of ice formation on surfaces with representative wettability, *Appl. Surf. Sci.*, vol.256, pp. 6764-6769, September 2010.
- [21] R. Karmouch, G.G. Ross, Experimental study on the Evolution of Contact Angles with Temperature Near the Freezing point, *J. Phys. Chem. C*, vol. 114, pp. 4063-4066, February 2010.