Bioinspired superhydrophobic surfaces on AA 6082 with improved corrosion resistance

A. Khaskhoussi, L. Calabrese, E. Proverbio

Despite the considerable demand for superhydrophobic surface (SHS) for different applications, it is still difficult to establish a suitable manufacturing process. In the present work, a simple strategy for SHS fabrication on AA6082 by consecutive hydrothermal treatment and silane coating was reported. The hydrothermal treatment duration showed an important influence on the morphology, wettability and corrosion resistance of the samples. The SEM showed the growth of a boehmite after the first few minutes of treatment. Increasing the time, the boehmite film became more dense and homogeneous. Thirty-minute sample showed the best wettability results (CA=180°; SA=0°) and an improvement of the corrosion resistance compared to bare aluminum (E_{corr} increased from -870 to -298mV and I_{corr} decreased from10^{-2} to 10^{-6}mA/cm^2). The SHS Bode plot showed two time-constants instead of one and the |Z| increased by one order of magnitude, due to the effective protective action of the SHS coating.

KEYWORDS: SUPERHYDROPHOBICITY; BOEHMITE, CORROSION, ALUMINUM ALLOY

INTRODUCTION

Overhead power lines are an important part of our electricity infrastructure networks. However, they are vulnerable to damages due to severe weather conditions. Rain and ice accumulation on conductors may lead to extensive mechanical damage, corrosion and significant levels of audible noise [1]. In particular, the corrosively of the atmospheres, which differs from soft (inland rural location) to highly aggressive (coastal location), strongly affects the aluminum conductors service life. Despite of their expected long service life (40 years), field data showed that the average service life of these aluminum conductors is between 10 and 20 years [2].The control of wettability behavior of the surfaces of high and medium voltage aluminum conductors can be an effective strategy to reduce the ice adhesion during a snowfall event and to avoid the water accumulation during rainy season. Indeed, hydrophobic and superhydrophobic surfaces and coatings can be used to protect the overhead lines and to increase their service life [3–5]. To this aim, in this work superhydrophobic surfaces on aluminum alloy were obtained coupling a hydrothermal treatment in order to create a nanoroughness to the aluminum substrates followed by a silanization step in order to deposit a low surface energy film. The immersion in boiling water (known as boehmitage) that is an easy and low cost hydrothermal

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treatment was used to obtain nanoscale roughness on aluminum alloy surfaces. The oxidative process leads, in few minutes, to the growth on the surface of a rough layer of boehmite. In particular, the effect of the hydrothermal treatment duration on the morphology, the anti-wetting properties and the anti-corrosion performances of the AA6082 aluminum alloy was investigated.

MATERIALS AND METHODS

Flat plates (24 x 40 x 2 mm) of the aluminium alloy (6082) were used as substrates. All the aluminium alloys samples were cleaned in ultrasonic bath for 5 minutes with acetone, bidistilled water and ethanol. The cleaned specimens were subjected to hydrothermal treatment by immersion in bidistilled boiling water for 1 min, 5 min, 10min and 30 min. Then, the boiled aluminium sample were dip-coated in Octadecyltrimethoxysilane /Toluene solution for 10 min. Afterward, the specimens were cured at 100°C for 3 hours. The curing parameters were optimized based on literature and preliminary tests performed in our laboratory. Morphologies were examined using a focused ion dual beam/scanning electron microscope (FIB-SEM ZEISS Crossbeam 540, ZEISS). Roughness details of the surfaces were conducted by performing AFM maps obtained by an Explorer microscope (Veeco Instruments, Munich, Germany) model MSCT-EXMT-BF1 and working in contact mode. The wettability of the coatings was evaluated using an Attension Theta Tensiometer equipment by Biolin Scientific according to sessile drop technique using 5 μL volume of distilled water at room temperature (25 ∘C). A micro CCD camera (Attension, Biolin Scientific) on site equipped recorded the images of the droplets to be further analysed using the software OneAttension V. 2.3 to obtain the static contact angles of droplets on each of the coatings. Measurements were replicated five times for each sample. Polarization and electrochemical impedance spectroscopy tests were performed, using a BioLogicSP-300 potentiostat, at ambient temperature in 3.5 wt.% NaCl solution (simulated seawater). A standard three-electrode cell, having a saturated Ag/AgCl electrode as the reference electrode, platinum wire as the counter electrode, and the superhydrophobic sample as the working electrode, were used. The exposed area of the working electrode was 1 cm^2.

RESULTS AND DISCUSSION

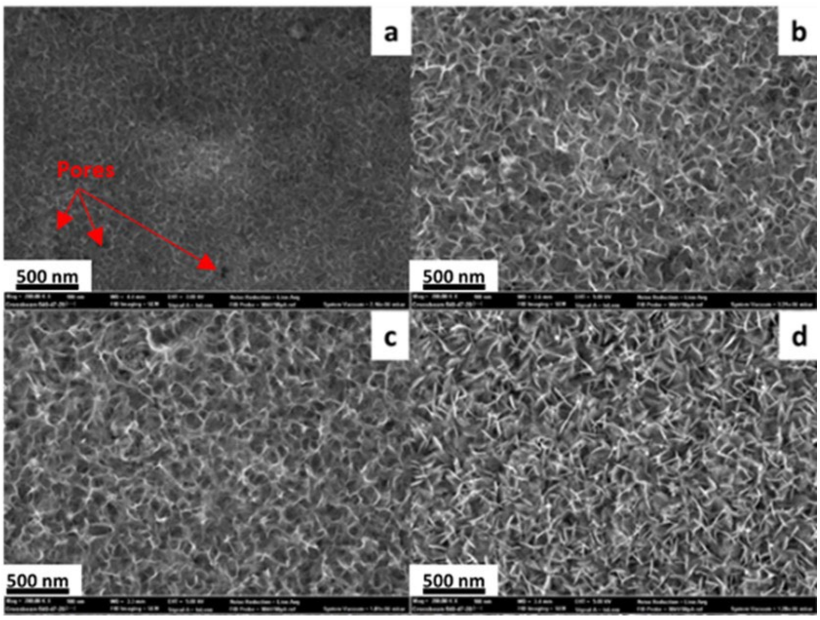

Fig.1 - SEM images after boiling treatment at different times: a) 1 min, b) 5 min, c) 10 min and 30 min

The surface morphologies of aluminum alloy surfaces immersed in boiling water at increasing time are shown in Figure 1. After 1 min of immersion in boiling water (Figure 1.a), the surface is fully covered by nanopores with thin boundaries and a thicker external film at the top of these nanopores. After 5 min of treatment (Figure 1.b), the surface appears with a quite homogenous flower-like nanostructure. Indeed, many 3D clusters grew on the aluminum alloy surface. These flower-like clusters are consisted of numerous petal-like flakes. As the immersion time increases (Figure 1.c,d), nano structural oxide layer increases in compactness and thickness. In fact, the neighboring platelets are overlapped and connected with each other inducing a thicker and more homogeneous film. In addition, a significant increase in density and a decrease in the porosity of the nanostructures can be clearly noticed. Thus, the density, the thickness and the homogeneity of this flower like layer can be controlled by changing the immersion time in bidistilled boiling water. This result is due to the formation of a protective film of aluminum oxyhydroxide layer with a boehmite crystalline structure (ɣ-AlO(OH)) [6,7]. As indicated in [8], the thickness of this film, obtained using various techniques has been estimated ranging from 200 nm to more than a micrometer by changing the treatment time in the range 0.5-240 min. In order to evaluate the effect of this aluminum oxyhydroxide film growth on the roughness of the surface, the height distribution on these surfaces was evaluated based on AFM mapping results as shown in Figure 2. The sample treated for 1 min is characterized by a wide and not regular height distribution ranged from 10 to 250 nm and a concentrated distribution from around 110 nm to 150 nm. This result is due to the presence of defects on the boehmite film such as nanoporosity and voids or local heterogeneity. Increasing the treatment time, the height distribution becomes less large and sharp. Furthermore, the surface roughness increases at increasing immersion time in boiling water. Indeed, after 30 min of hydrothermal treatment, the distribution is restricted and concentrated between 280 and 290 nm.

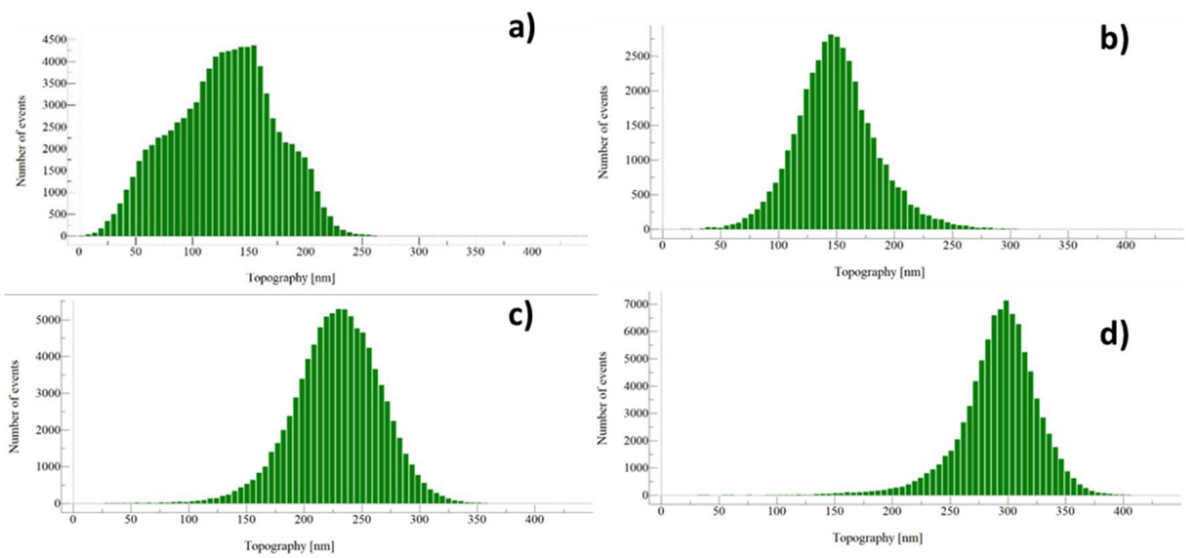

Fig.2 - Histograms of height distribution of samples treated at different times after silanization: a) 1 min, b) 5 min, c) 10 min and d) 30 min.

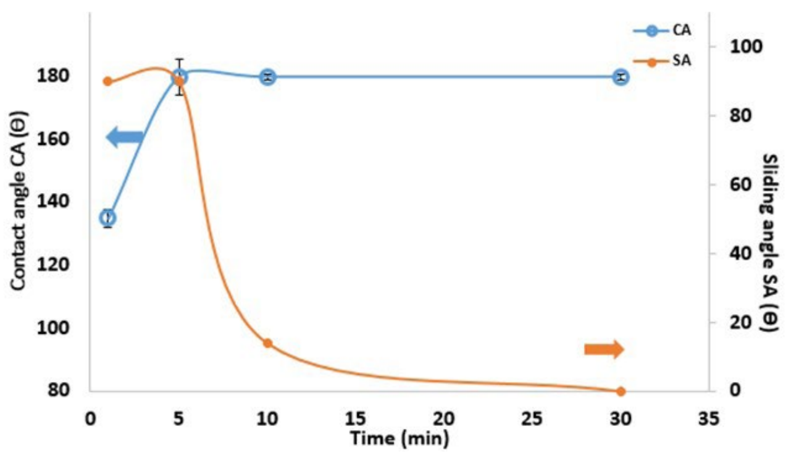

Fig.3 - Static water contact angles and sliding angles vs. immersion time in boiling water.

Figura. 3 shows the evolution of the static water contact angle and the sliding angle values of treated aluminum surfaces as a function of immersion time. The water contact angle was about 137.5 ± 3° for a 1 min immersion time. By increasing the immersion time, the contact angle increased gradually, and for immersion time of more than 10 minutes, the contact angle reached 180°. Measurement of the sliding angle is essential to characterize the superhydrophobic surface. For example, a water droplet on a horizontal surface with a high contact angle can remain attached until the surface is tilted to a considerable angle [9]. Consequently, the contact angle alone is not enough for reflecting the wettability behavior of a solid surface. Wenzel and Cassie-Baxter are the two main models that describe the wetting behavior based on contact angle and sliding angle. According to Wenzel's model, the liquid droplet maintains contact at all points with the solid surface below it. However, in Cassie-Baxter state, the air pockets are entrapped in the surface cavities, resulting in a composite liquid-solid-air interface inducing a low liquid adhesion on the solid surface. As shown in Fig. 3, the samples treated for 1 min and 5 min are characterized by extremely high sliding angle of about 90° indicating that these samples follow the Wenzel state. Increasing the immersion time, above 5 min, a transition from Wenzel to Cassie-Baxter state occurred that manifested in the radically decrease of the sliding angle. In particular, the sliding angle reached a value of about 0° after 30 min of treatment.

The increase in static contact angle and the decrease of the sliding angle could be explained by the increase of roughness and the variation of surface morphology during the boehmite film growth. As shown in Fig. 2, The surface roughness becomes higher and the height distribution becomes more limited which is due to the suppression of porosity and the evolution of the flower like structure at high treatment time. Indeed, the more the boehmite film is homogeneous and rough the higher the surface contact angle is obtained. In addition, the sharp edges of the flower-like structure observed for immersion times of 10–30 minutes may serve as a means of trapping sufficient air solid-liquid-air interface which increase the liquid-air interfacial ratio and decrease of the liquid-solid interfacial ratio inducing the transition from Wenzel to Cassie-Baxter state. This transition induces a diminution of the water adhesion on the treated AA6082 surface and the reduction of water sliding angle. In particular, on the surface on the sample immersed for 30 min in boiling water, the water droplet spontaneously rolls off without any tilting of the sample [10].

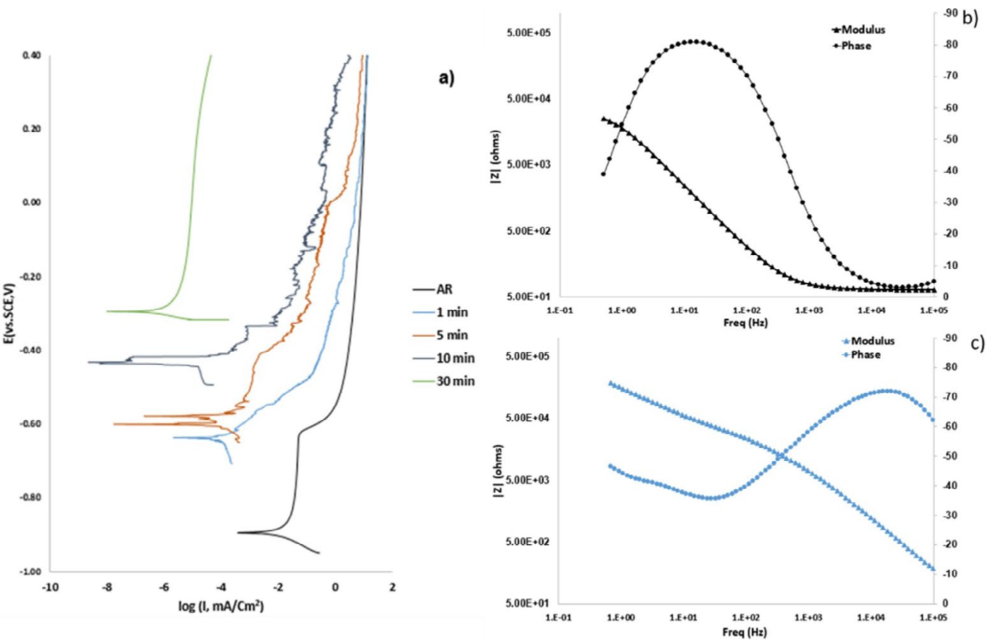

Fig.4 -Electrochemical polarization curves of the as received AA6082 and the treated surfaces at different times (a) and bode plots of the as received AA6082 (b) and the superhydrophobic AA6082 sample treated at 30 min (c) in simulated seawater.

Figure. 4. a. shows the polarization curves of as received and treated AA6082 surfaces. As shown, in the polarization curves, the proposed SHS treatment of the aluminum surface significantly improves its corrosion resistance. Indeed, the corrosion potential of the as-received sample is −870 mV vs. SCE. Due to the surface modification, the corrosion potential Ecorr shifted toward noble potentials. In fact, Ecorr positively increases from −870 mV to −644 mV for 1 min sample, up to about -595 mV and -431 mV for 5 min and 10 min samples, respectively. Afterwards, E_{corr} decreases again to reach -298 mV for the 30 min sample. In addition, the increase of the duration of the surface treatment of the AA6082 aluminum surface induced a gradual decrease of the corrosion current density (calculated using the Tafel method) from around 10^{-2} mA/cm^2 to around 10^{-6} mA/cm^2. These results are consistent with the wettability results. In particular, the best corrosion results were obtained with the superhydrophobic surfaces following the Cassie-Baxter state (30 min samples). The superhydrophobic surface reduced the interaction between the simulated seawater solution thus enhancing the corrosion resistance of the samples. Indeed, the trapped air on the flower-like nanostructure of the salinized boehmite layer of the AA6082 superhydrophobic surface acts as an "air cushion" preventing the diffusion of corrosive ions (Cl-) and thus improving the corrosion protection [9]. In order to provide more information about the structure and the properties of these surfaces, electrochemical impedance spectroscopy tests were carried out on the as received and treated AA6082 samples. As reference, in Figure. 4. b,c the comparison of Bode plot for the as received aluminum and 30 min samples is reported. The surface modified sample is characterized by a relevant increase in the impedance modulus in all frequency ranges. In particular, at low frequencies, the |Z| is at least an order of magnitude greater than that the as received AA6082. It is well known that higher |Z| modulus at lower frequency reveals an improved corrosion resistance on metallic substrate [11].The Bode phase plots of the as received AA6082 present only one time constant at intermediate frequencies (10^1-10^2Hz) that is typical of the resulting oxide layer naturally formed due to the corrosion of the AA6082 surface in the electrolyte. Instead, the Bode phase plots of superhydrophobic surface show an additional time constant at high frequencies due to the barrier action provided by superhydrophobic film formed on the AA6082 substrate. Thus, the different morphologies of oxide layer in terms of density and roughness, generated by different boiling duration, have a relevant influence on the AA 6082 corrosion resistance.

CONCLUSION

In summary, we develop a novel, economic and safe hydrothermal strategy to give a superhydrophobic performances to aluminum alloy. The effect of the duration of the hydrothermal treatment of the morphology, the wettability and the corrosion behavior of the AA6082 was investigated. A nanometric structure was spontaneously generated in boiling water. Density and porosity of this structure can be optimized increasing the treatment time. A direct relationship between the immersion time, the roughness and the anti-wetting behavior was highlighted. The results of electrochemical tests indicate that the as prepared aluminum alloy exhibits good anti-corrosion behavior in 3.5% NaCl solution compared to the as received one and that its corrosion increases with the treatment time. The reported hydrothermal approach offers an effective strategy for the large-scale production and extends the potential applicability of AA6082 in the near future.

REFERENCES

[1] Q. Li, R. Shuttleworth, G. Zhang, I. Dupere, S.M. Rowland, Acoustic noise evaluation for overhead line conductors, in: 2013 IEEE Electr. Insul. Conf. EIC 2013, 2013: pp. 119–123.
[2] W.G. B2.44, Coatings for Protecting Overhead Power Network Equipment in Winter Conditions, in: CIGRE631, 2015.
[3] A. Khaskhoussi, L. Calabrese, E. Proverbio, Superhydrophobic Self-Assembled Silane Monolayers on Hierarchical 6082 Aluminum Alloy for Anti-Corrosion Applications, Appl. Sci. (2020) 1–14.
[4] L. Calabrese, A. Khaskhoussi, S. Patane, E. Proverbio, Assessment of Super-Hydrophobic Textured Coatings on AA6082 Aluminum Alloy, Coatings. 9 (2019) 352.

[5] C. Lian, C. Emersic, F.H. Rajab, I. Cotton, X. Zhang, R. Lowndes, L. Li, Assessing the Superhydrophobic Performance of Laser Micropatterned Aluminium Overhead Line Conductor Material, IEEE Trans. Power Deliv. (2021).

[6] A.C. Geiculescu, T.F. Strange, A microstructural investigation of low-temperature crystalline alumina films grown on aluminum, Thin Solid Films. 426 (2003) 160–171. doi:10.1016/S0040-6090(02)01293-2.

[7] A.N. Rider, The influence of porosity and morphology of hydrated oxide films on epoxy-aluminium bond durability, J. Adhes. Sci. Technol. 15 (2001) 395–422.

[8] Z.S. Saifaldeen, K.R. Khedir, M.F. Cansizoglu, T. Demirkan, T. Karabacak, Superamphiphobic aluminum alloy surfaces with micro and nanoscale hierarchical roughness produced by a simple and environmentally friendly technique, J. Mater. Sci. 49 (2014) 1839–1853.

[9] A. Khaskhoussi, L. Calabrese, E. Proverbio, Effect of the Cassie Baxter-Wenzel behaviour transitions on the corrosion performances of AA6082 superhydrophobic surfaces, Int. J. Ital. Assoc. Metall. 113 (2021) 15–21.

[10] B. Zhang, Y. Zeng, J. Wang, Y. Sun, J. Zhang, Y. Li, Superamphiphobic aluminum alloy with low sliding angles and acid-alkali liquids repellency, Mater. Des. 188 (2020) 108479.

[11] B. Zhang, J. Wang, J. Zhang, Bioinspired one step hydrothermal fabricated superhydrophobic aluminum alloy with favorable corrosion resistance, Colloids Surfaces A Physicochem. Eng. Asp. 589 (2020) 124469.