Nanocoating on aluminium alloy with self-cleaning and icephobic performances for anti-corrosive applications

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This work seeks to develop a low-cost superhydrophobic coating on 6082 aluminium alloy using a simple and safe method. The method consists of a combination of surface nanostructuration with the chemical grafting of silane molecules. AA 6082 substrates have been subjected to hydrothermal roughening. Then, these surfaces have been subjected to a grafting treatment with low surface energy silane.Through the applied methodology, it was possible to obtain nanoroughness coating with a high contact angle (>150°) and a low sliding angle (<5°). The evaluation of ice resistance, corrosion resistance and self-cleaning were carried out. The results reveal that the corrosion resistance of the coated aluminum alloy was much better than the substrate in coca cola. Different types of dust particles were easily removed by the rolling motion of droplets confirming the self-cleaning performance of the obtained nanocoating. A comparative analysis of the anti-icing properties of the aluminum alloy surface before and after treatment showed an outstandingly better performance for the nanocoated surfaces. Indeed, a reduction of ice adhesion by about 40% was observed. These multifunctional coatings hold high potential for application in several fields, ranging from food safety to medical field, offering sustainable and safe solutions.

KEYWORDS: BEARING STEELS, AUSTEMPERING, MICROSTRUCTURE, HARDNESS, BAINITE

INTRODUCTION

Aluminum and its alloys are common industrial metals, especially in food and beverage packaging. Indeed, since the invention of the metal cans, more than 250 billion of them are produced annually [1].The inclusion of more electropositive components in soft drinks eases the corrosion of aluminum. Oxygen concentration in the package; pH; product composition; dissolved salts, ions, and molecules; and the environment, temperature, and pressure all affect metal corrosion. For instance, drinks with a low pH can dissolve the aluminum oxide layer, which serves as a natural passivation layer. Leaking metal ions from cans into drinks can cause serious illness such as Parkinson's, Alzheimer's, and multiple sclerosis. Thin-layer coatings are used for can to reduce metal-product contact and improve corrosion protection including vinylic or phenolic lacquers and epoxy resins. Epoxy resins are used in advanced polymer materials because of their thermal, mechanical, and corrosion resistance [2]. Epoxy in the can's interior coating keeps canned goods

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fresh [3]. This type of material must be inert enough not to harm human health or reduce food quality [3]. However, Several researchers found that epichlorohydrin and bisphenol A (BPA) can leach into food or drinks from epoxy coatings which have a grave biological impacts and health concerns [4]. In fact, numerous published studies showed that the BPA exposure can cause reproductive system abnormalities, cardiovascular illness, and nervous system development [5]. New research has also linked BPA to hypertension, type 2 diabetes, and cardiovascular disease [6]. A stratagem to overcome these issues is to design smart surfaces to prevent or inhibit the surface/food contact. One of these smart surfaces is the superhydrophobic one [7].

The superhydrophobic property corresponds to a surface whose static water contact angle is > 150°. This effect is generated through combining micro/nanostructure with surface modification of highly nonpolar ligands [8]. Chemical and physical vapor deposition, layer-by-layer, electrospinning, etching, and sol-gel chemistry are the most common strategies studied by researchers for fabricating the superhydrophobic surfaces [9]. There are several complications which preclude the immediate and widespread use of superhydrophobicity in the food industries. The techniques used to fabricate these surface coatings are often technically complex, difficult to implement and cost effectively at large scale. Similarly, the precursors required for the surface modifications can be expensive and harmful. In this sense, the present work aimed to obtain a low-cost superhydrophobic coating on 6082 aluminum alloy, with low interaction with soft drinks as well as evaluating its wettability, self-cleaning and anti-corrosive and low ice adhesion properties. The selected beverage is coca cola that is one of the most consumed soft drinks in the world. Cola soft drinks contain carbonated water, sugar, caffeine, extract of the cola nut, caramel coloring, acidulant (phosphoric acid) and natural flavoring compounds [10] and it is characterized by highly acidic pH making of it a very aggressive liquid for aluminum.

MATERIALS AND METHODS

Flat plates (24 x 40 x 2 mm) of hot rolled aluminum plates (6082) were used as substrates. All the aluminium alloys samples were cleaned with acetone, bidistilled water and ethanol in ultrasonic bath for 5 minutes and dried at room temperature. The cleaned samples were pretreated by immersion in boiling water for 1 min, 5 min, 15 min. After that, the as treated specimens were immersed in Octadecyltrimethoxysilane/Toluene solution for 10 min. Afterward, the specimens were cured at 100°C for 3 hours. The curing temperature and time were optimized by preliminary tests performed in our laboratory. Morphologies were examined using a focused ion dual beam/scanning electron microscope (FIB-SEM ZEISS Crossbeam 540, ZEISS). The wettability of the coatings was evaluated using an Attension Theta Tensiometer equipment by Biolin Scientific according to sessile drop technique using 3 μl volume of distilled water at 25 ∘C. The images of the droplets were recorded by a micro CCD camera (Attension, Biolin Scientific) and analyzed by software OneAttension V. 2.3 to obtain the static contact angles. Measurements were replicated five times for each sample. Ice adhesion properties were evaluated by shear stress analysis performed with a home-made mold using a universal testing machine (Lloyd EZ 50). Aluminum alloy samples were used as test samples; they were frozen in mold, in 40 ml of deionized water at −19 °C for 48h. Afterwards, the mold was fixed into the machine and the sample was extracted from the ice at a speed of 3 mm/min. The force F needed to pull the sample off the mold was recorded and converted to shear stress. The shar stress was calculated as the average of 3 tests carried out on 3 different specimens.

Polarization and electrochemical impedance spectroscopy tests were performed, using a BioLogicSP-300 potentiostat, at ambient temperature in Coca-Cola. 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, was used. The exposed area of the working electrode was 3.14 cm^2.

RESULTS AND DISCUSSION

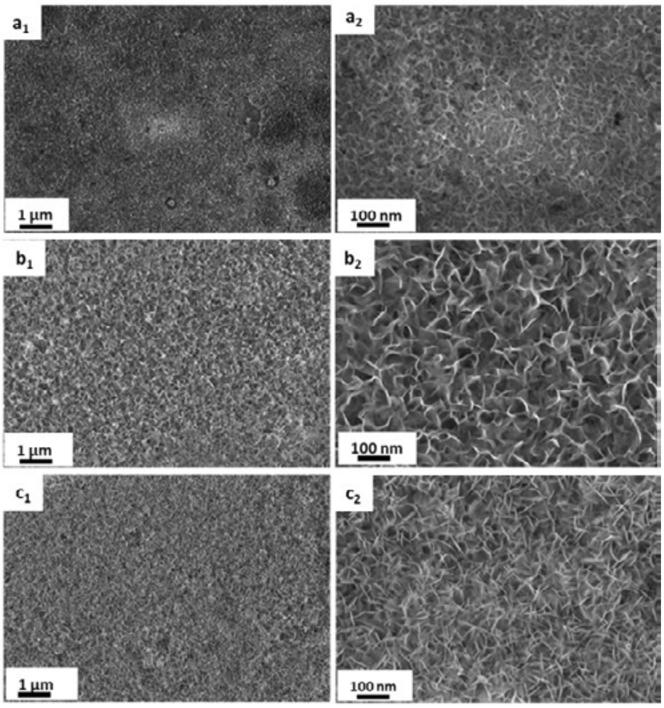

Fig.1 - SEM images after boiling treatment at different times: ai) 1 min, bi) 5 min and ci) 15 min (with index 1 for microscale, index 2 for nanoscale) / Immagini SEM dopo il trattamento in acqua bollente per tempi differenti: ai) 1 min, bi) 5 min e ci) 15 min (indice =1 per microscala, indice=2 per nanoscala).

Figure 1 displays the SEM images of the surface after the treatment in boiling water at different times. At short immersion time (1 min), it is possible to observe at Figure 1ai, the presence of thin, porous layer distributed along the aluminum surface. Increasing the immersion time to 5 min (Figure 1bi), the surface appears with a quite homogenous 3D flower-like morphology. This flower-like structure is formed by nano petals with a thickness of about 5 nm and a length of 50 to 80 nm. A further increase of the immersion time to 15 min, induces the overlapping and the connection of these petals resulting in a thick, compact, and homogeneous surface film. Thus, a significant increase in density, homogeneity, and a decrease in the porosity of the nanostructured film on aluminum surface can be obtained by increasing the immersion time in boiling water. This is due to the fact that the aluminum is able to form, in boiling water, a protective film which was identified as aluminum oxyhydroxide layer having the boehmite crystalline structure (ɣ-AlO(OH)) [11,12]. In order to evaluate the effect of this film on the wettability of aluminum surfaces, the water contact angle and sliding angle measurements were conducted.

Figure 2 shows the photos of the static contact angle and the sliding angle of water droplets on silanized aluminum surfaces at different immersion time in boiling water. The water contact angle was about 137.5° for 1 min immersion and the droplet adhesion to the surface was extremely high. This result is due to the presence of defects on the boehmite film such as nanoporosity and voids or local heterogeneity.

Increasing the immersion time to 5 min, the contact angle increased to reach 174° but no significant improvement was observed in the sliding angle.

This behavior indicates that the samples 1 min and 5 min are following the Wenzel state. The Wenzel state can be defined as a wet contact mode in which the water droplet totally penetrates the surface asperities and the triple-phase air/liquid/solid contact line is stable and regular. Wenzel's state is also known as homogeneous wetting which explains the high-water adhesion on the surface.

An additional increase in treatment time to 15 min induced a dramatical decrease of the sliding angle. This low water adhesion can be explained by the heterogeneous wetting theory proposed by Cassie. In Cassie's theory, the liquid does not wet the surface valleys because of the trapped air, so the grooves and peaks in the surface profile are in contact with the air and the liquid, respectively. In such a configuration, thanks to the high effective combined action of the silane low energy and the homogeneous nanostructure, pockets of air can be stably entrapped in the water/substrate interface, significantly reducing the contact area between the solid and the water droplet inducing an easy water sliding.

The increase in static contact angle and the decrease of the sliding angle could be explained by the modification of the surface morphology during the boehmite film growth. As shown in Figure 1, the suppression of porosity and the evolution of the flower like structure at high treatment time results in the formation of superhydrophobic surface. In fact, the more the boehmite film is homogeneous and rough the higher is the water repellency. In fact, the sharp edges of the flower-like structure observed on the 15 min sample improved the air trapping forming a homogenous air layer on the solid-liquid interface inducing the transition from Wenzel to Cassie-Baxter state.

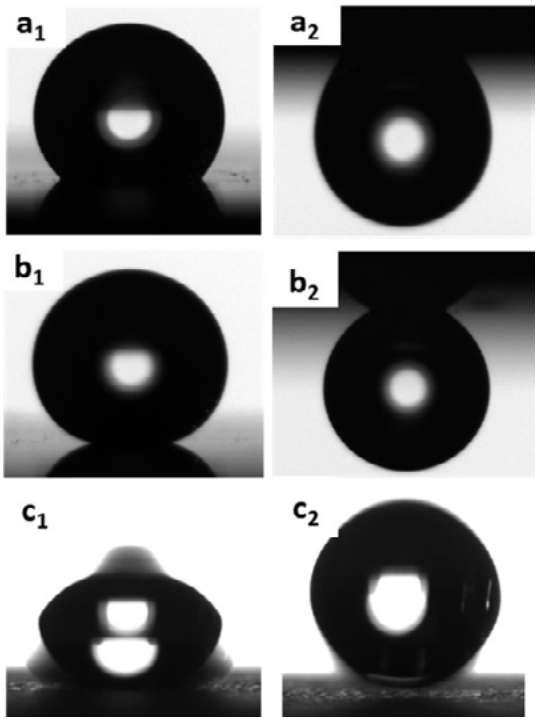

Fig.2 - Measurements of water contact angles (a1: 1 min, b1: 5 min and c1: 15 min) and Sliding angles (a2: 1 min, b2: 5min and c2: 15 min) on the surface of the silanized aluminum after boiling at different times / Misurazioni dell'angolo di contatto con acqua (a1: 1 min, b1: 5 min e c1: 15 min) e dell'angolo di scorrimento (a2: 1 min, b2: 5 min e c2: 15 min) sulla superficie dell'alluminio trattato per tempi differenti.

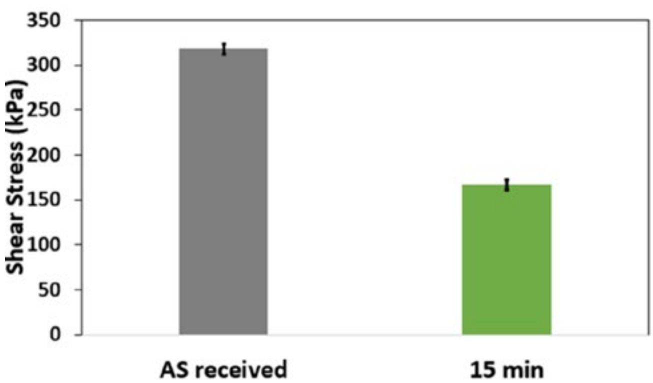

Fig.3 - Shear stress of ice on the surface of aluminum before and after treatment / Sforzo di taglio di scorrimento all'interfaccia ghiaccio-superficie di alluminio prima e dopo il trattamento.

Ice adhesion tests were carried out on the as received and treated aluminum alloy for 15 minutes which was characterized by the best anti-wetting performances. The superhydrophobic surface showed a lower ice adhesion than the untreated one (Figure 3). A reduction of about 47% of the shear stress was obtained by treating the aluminum indicating that the homogeneous nanotextured salinized oxide film plays an important role in lowering the ice adhesion.

Figure 4. illustrates the polarization curves of untreated and treated aluminum alloy surfaces with the photos of the surfaces after linear polarization. Measurements were performed in commercial coca cola without removal of CO_2 to try to reproduce the service life of the product. The CO_2 can be degassed during the experiment and can be replaced by O_2, accelerating corrosion by contributing to the cathodic reaction of oxygen reduction in acidic media [13]. The curves show that the superhydrophobic sample presented lower current density (i_{corr}) and more positive corrosion potential (E_{corr}) to the as received one, indicating a reduction in the corrosion-dynamic rate and the corrosion thermodynamic tendency, respectively [14]. The corrosion potential of the as-received sample is −580 mV vs. Ag/AgCl. Thanks to the surface treatment, the corrosion potential E_{corr} shifted toward positive potential. E_{corr} positively increases from −580 mV to -100 mV for 15 min sample.

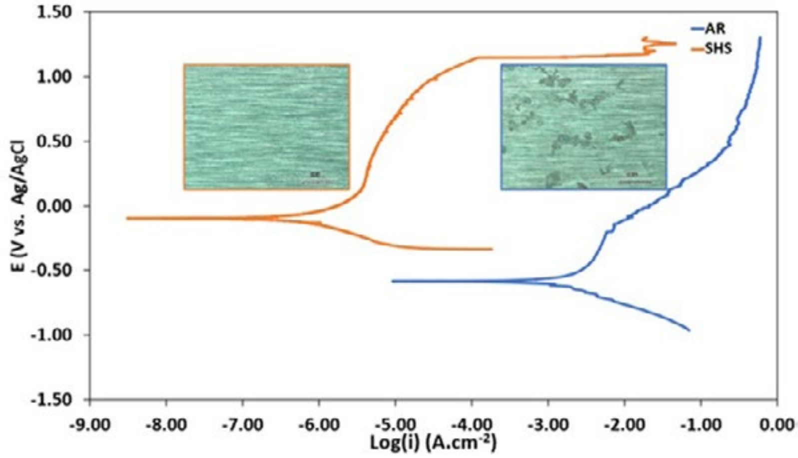

Fig.4 - Polarization curves of the coated and uncoated aluminum / Curve di polarizzazione dell'alluminio rivestito e non rivestito.

In addition, the applied surface treatment of the AA6082 aluminum surface induced a decrease of the corrosion current density from around 1.32 μA/cm² to around 6.36 10^{-6} μA/cm². These results are consistent with the wettability results. Indeed, the corrosion resistance followed the order sample 15min>5min>1min> as received. For brevity reason, the tests of 1min and 5min samples were not reported in the paper.

The superhydrophobic surface reduced the interaction between the coca cola and the aluminum alloy, preventing the diffusion of corrosive ions and thus improving the corrosion resistance of the samples. The trapped air on the flower-like nanostructure of the aluminum oxyhydroxide layer acts as an "air cushion" preventing corrosion. The images of the two surfaces after polarization confirmed that there is a significant difference between the two surfaces. The superhydrophobic surface seems unmodified. However large areas of corrosion were observed on the SHS surface. These results confirm that the air layer was stabilized within the rough grooves of the superhydrophobic surface throughout the whole experiment.

Because of its adaptability and precision, electrochemical impedance spectroscopy (EIS) is frequently used in corrosion studies to examine the corrosion performance of coated metals [15]. EIS measurements were conducted in coca cola for the aluminum before and after treatment.

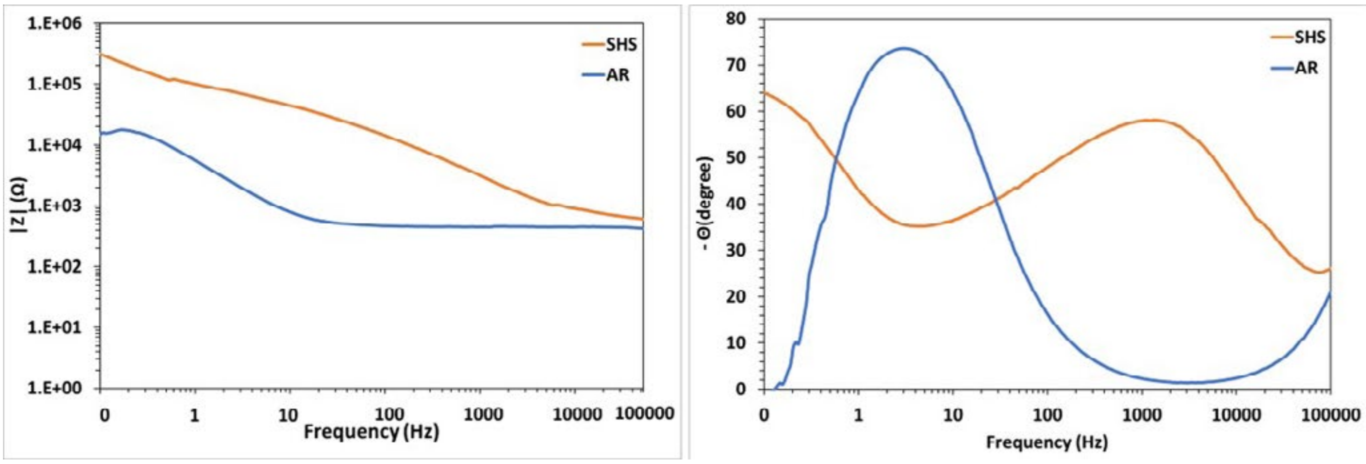

Fig.5 - Electrochemical impedance spectra: As received (AR) and superhydrophobic aluminum (SHS) / Spettri di impedenza elettrochimica: come ricevuto (AR) e alluminio superidrofobico (SHS).

The comparison of Bode plots for the as received aluminum and superhydrophobic sample is reported in Figure 5. The surface modified sample is characterized by a relevant increase in the impedance modulus in all frequency ranges. At low frequencies, the |Z| is extremely higher than the untreated sample. It is well known that higher |Z| modulus at lower frequency reveals an enhanced corrosion resistance on metallic sample. The Bode phase plots of the as received AA6082 present only one time constant at intermediate frequencies (10^{-1}-10^{2}Hz) that is typical of the resulting oxide layer naturally formed due to the corrosion of the aluminum surface. Instead, the Bode phase plots of superhydrophobic surface shows two-time constants. The one at high frequencies is due to the barrier action provided by superhydrophobic film formed on aluminum surface. These results confirm the good barrier action of the obtained superhydrophobic surface in aggressive environment like the cola carbonated beverages that contain phosphoric acid as the acidulant and therefore have low pH value (2.50) and have high conductivity (1048 μS), a high level of dissolved CO_2 (3.6) and a higher soluble solid content [13].

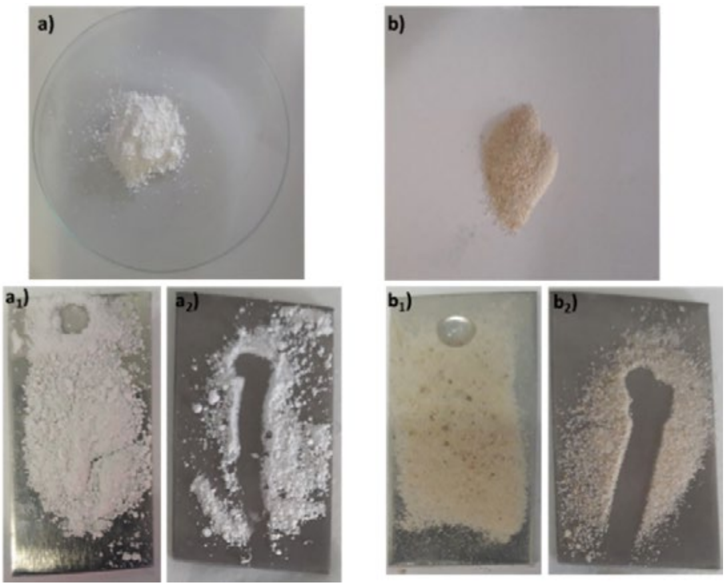

Fig.6 - Self-cleaning behavior of the superhydrophobic surfaces using two contaminants: (a) alumina powder and (b) sand on as received aluminum (a_1, b_1) and superhydrophobic surface (a_2, b_2) / Comportamento autopulente delle superfici superidrofobiche utilizzando due contaminanti: (a) polvere di allumina e (b) sabbia silicea su alluminio non trattato (a_1, b_1) e superficie superidrofobica (a_2, b_2)

A low sliding angle is necessary to promote the self-cleaning capability of a surface. Self-cleaning property can be evaluated by a water rolling test on randomly spread dust on the superhydrophobic surface. Two types of powder were used as contaminants: sand and alumina powder (Figure 6). The powders were distributed on the 15 min superhydrophobic surface, then exposed to water droplets using a pipette. When the water droplets encountered the powder particles, the powders were picked up immediately leaving a clean surface and confirming the potential self-cleaning capability of this developed superhydrophobic coating.

CONCLUSION

At the end this study, it is possible to conclude that:

- Superhydrophobic coatings on AA6082 with self-cleaning properties were obtained following a low-cost and economically viable methodology by optimizing the immersion time in boiling water and silanization.
- Homogeneous Flower-like nanostructure generated by immersion in boiling water for 15min, followed by a simple deposition of silane layer on AA6082 induced a high repellence effect with CA= 180 and SA=0.
- A significant reduction of around 40% of ice adhesion was achieved.
- An improvement of the corrosion protection was achieved thanks to the formation of the air layer on the nanostructured superhydrophobic surface.

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