



A study of the mechanical and chemical durability of Ultra-Ever Dry Superhydrophobic coating on low carbon steel surface



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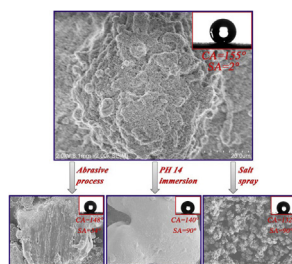
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HIGHLIGHTS

- Mechanical and chemical durability of Ultra-Ever Dry Superhydrophobic coating were systematically evaluated.
- XPS and SEM have been conducted to analyze the cause of the change in wettability of the SH surface under mechanical and chemical test environment.
- The corrosion process of salt spray induces pit-etching, which can result in the loss of superhydrophobicity due to the appearance of Fe-O nanoplates with high surface energy.
- A new simple method has been proposed to repair the superhydrophobicity which has been degenerated due to rusting caused by salt spray.

GRAPHICAL ABSTRACT



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ABSTRACT

Both mechanical and chemical durability of superhydrophobic (SH) surfaces are very important properties for industrial applications. In this paper, the durability of the Ultra-Ever Dry, as a commercial SH product, sprayed onto low carbon steel has been systematically studied by sand paper abrasion, waterfall/jet test and immersion in solution of different pH values as well as salt spray test. The results show that the degeneration of superhydrophobicity of the coating during the abrasion was mainly due to the loss of both the top layer of micro-scale bumps and their nanoparticles (NPs). Waterfall/jet impact could also cause the loss of NPs on the micro-scale bumps of the coating, which corresponds with the change of wettability. Different chemical processes elicit complex effects on the SH Surface. The coating is able to maintain its superhydrophobicity in solutions of pH 1–12, whereas a solution of pH 14 causes both chemical change and loss of NPs, and as a result, the loss of the water-repellent property. The salt spray test shows that the pitting corrosion on the surface and the degeneration of superhydrophobicity are mainly induced by morphological and surface chemical changes

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such as the formation of new Fe-O nanostructures that presented as pit-etching on the coating surface. The results also confirm that superhydrophobicity degeneration of the SH coating surface by salt spray can be easily recovered through treatment with fluoroalkylsilane (FAS-17).

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1. Introduction

Superhydrophobic surface, with a water contact angle greater than 150° and a sliding angle less than 10° , has attracted tremendous attention due to its potential applications in self-cleaning [1–3], anti-icing [4,5], anti-fouling [6,7] and anti-corrosion [8–10]. Presently, countless methods of SH surface have been reported in the literatures. However, facing with the challenge of practical application, an overwhelming majority of SH surfaces are still stuck in laboratory due to the complex preparation process and their poor durability (i.e., their superhydrophobicity cannot persist for a long time and/or in particular environmental conditions). These issues may be attributed to the fact that the micro/nanostructures, an essential part of SH surface, are inherently fragile. Despite the difficulties mentioned above, a few companies recently managed to launch their SH products into the market. These products include Ultra-Ever Dry (Ultratech International, USA) [11], Supercoat (Wuxi Shunye Technology, China) [12] and Never-Wet (NeverWet LLC, USA) [13]. These SH coatings may (or should) have a better durability as they are commercial products for practical applications. Hence, a systematic study of their mechanical and chemical durability should provide valuable information that may be of significance for people to perform and compare research on SH surfaces in the future.

Recently, many researchers have paid much attention to enhancing the durability of SH surfaces [14–28]; however, the results cannot be easily compared due to the different evaluation methods or the same evaluation method conducted with various procedures. In addition, there is still no standard sample available for a proper comparison. A valid and recognized standard for evaluating the durability of SH surface has yet to be established at present. These issues were comprehensively reviewed and discussed by Milionis et al. [14], and Malavasi et al. [15], in their recent papers.

In general, mechanical durability of a SH surface is widely measured by means of abrasion wear [16–27] and water jet/fall impact [28–34]. The chemical durability of a SH surface is extensively evaluated by immersion of varying pH solutions [35,36] and electrochemical corrosion test [8,37,38]. Results demonstrate that most of the SH surfaces show better corrosion resistance based on immersion in different pH solutions and electrochemical test; however, it may not be enough for practical applications. A SH surface repels liquid by air underneath the liquid, but not necessarily moisture. Thus for the surface of SH coatings, we need to consider the effects of moisture. The salt spray test which provides a controllable moisture environment has been intensively used as corrosion evolution of coatings in industry [39]. Through the salt spray test, one can determine the relative corrosion-resistance information of various materials including coatings. However, there has been very few reports on SH coatings that underwent the salt spray test despite the fact that superhydrophobic coatings were described as an excellent corrosion protection.

In this work, we have systematically studied the durability of Ultra-Ever Dry as a commercially available SH coating. With our results, we aim to provide an important and independent evaluation of the performance of this commercial SH coating protocol as a standard sample for comparison and reference data for future

Table 1

Chemical composition of the low carbon steel in this work.

Elements	C	Mn	S	P	Si	Fe
Content (%)	0.13	0.60	0.05	0.015	0.01	residue

SH surface evaluations. The mechanical durability of the Ultra-Ever Dry coating was first evaluated by abrasion wear test with sandpaper and water fall/jet test, their degeneration mechanisms have been studied based on the change of the surface chemical composition and morphology. The chemical durability of the coating was characterized by immersion in solutions with different pH and salt spray test. The change of surface morphology was detected and analyzed from SEM. Surface chemistry has been comprehensively studied using XPS. Lastly, we found that the loss of superhydrophobicity of the SH surface induced by salt spray can be easily repaired due to the new nano/micro structures formed during the salt spray.

2. Materials and methods

2.1. Materials

Ultra-Ever Dry was purchased from Ultra Tech International, Inc. with 1LB bottom packages both 4000(bottom coating) and 4001(top coating). The substrate, a low carbon steel (120 mm length \times 50 mm width \times 0.28 cm thickness), was purchased from Wuxi Guangyuan Auspicious Metal Materials Co., Ltd., and its nominal compositions are listed in Table 1. The surface was successively polished using sandpaper of different grades (e.g., 200#, 600# and 1200#), cleaned by sonication in ethanol for 5 min and quickly dried by an air blower. For fear of potential corrosion, the edges and the other side of the substrate were protected by tape. According to the instructions, the coatings were sprayed onto the substrate as shown in Fig. S1 of the Supporting information. Finally, samples were kept at room temperature for 24 h prior to testing. The thickness of coating was measured by coating thickness gauge GTS810F (Guangzhou Guo ou electronic Co., Ltd.), the average thickness of the sprayed coating is $45 \mu\text{m}$.

2.2. Characterizations and tests

2.2.1. Surface morphology and chemical composition

Surface morphology of samples was characterized by a Hitachi S-4800 scanning electron microscopy with field emission electron gun. The X-ray photoelectron spectroscopy (XPS, PHI5000 Versa scanning probe-II XPS Microprobe system, with Al $K\alpha$ monochromatic X-ray source) was used to study the surface chemical composition. The survey spectra have been carried out with 100 eV pass energy and 1 eV step. High spectra was acquired at 20 eV pass energy and 0.05 eV step. All peaks were calibrated using C1s = 284.6 eV. High resolution XPS spectra were deconvoluted by CASA XPS.

2.2.2. Wettability of surface

Contact angles were measured using a SL200B Static and Dynamic Optical Contact Angle Goniometer (USA Kino Industry Co., Ltd.) with an accuracy of $\pm 1^\circ$. The sessile drop method was used to

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