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Durable, superhydrophobic, superoleophobic and corrosion resistant coating on the stainless steel surface using a scalable method

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ABSTRACT

In this study, superamphiphobic coating was produced using low surface energy materials and fabrication of hierarchical structures on stainless steel surface. Hierarchical structure was fabricated by silica multilayer coatings and adequate control of particles size in each layer. The surface energy was decreased by fluoropolymer compounds. The maximum static contact angle of DI water, ethylene glycol and fuel oil droplets on the prepared surface increased from 64° to 166°, from 33° to 157° and from 0° to 116°, respectively. Also, the minimum sliding angles of DI water, ethylene glycol and fuel oil droplets on the prepared surface were less than 2°, 5° and 12°, respectively. These results confirmed the superhydrophobicity and superoleophobicity of coated surfaces. These films maintained their superamphiphobicity after 16 days of immersion in water. In electrochemical corrosion evaluation, the highest protection efficiency of fabricated films reached as high as 97.33%. These satisfied results confirmed that this simple method can be used to fabricate large scale samples.

1. Introduction

Adhesion and friction are major problems limiting both the production yield and the useful life time of equipments in several industries. This problem sometimes leads to change of pieces and stop of process that are costly. A new method for reducing of this problem is anti-stiction coatings. The surfaces coated by these materials have low wettability, high self-cleaning property and low resistance against flow. Non-wettability is one of the crucial surface properties for materials in a number of potential applications, including separation of oil/water dispersions, drag reduction, anti-fouling, anti-icing, stain-resistant surfaces [1–6]. Oleophobic surfaces may have more wide applications than the hydrophobic surfaces. Resistance against wax deposition in petroleum industry is an important application of superoleophobic surfaces [7–10]. Because of the low surface tension of most oils, creating superoleophobic surfaces with high static contact angles (CAs) and low sliding angles (SAs) of oil droplets is much more difficult than creating superhydrophobic surfaces [4,7,11–16].

The phenomenon of non-wettability is generally found in nature such as lotus leaves, butterfly's wing, water strider's legs, desert beetle's backs, skins of fish and shark and so on [3,7,9,13,14,17–20]. Inspired by the amazing wettability of these natural species, many artificial superhydrophobic surfaces have been fabricated but there are very few reports of an artificial surface with superoleophobic property [11,15]. The wettability of solid substrates is known to be dependent on both their chemical composition and their topographic structure. In this regard, a combination of surface roughening and lowering the surface energy affords the liquid repellency [2–6,8,13–15,20–26]. It has been reported that the lowest surface energy groups in monolayer films have an order $-CH_2 > -CH_3 > -CF_2 > -CF_2H > -CF_3$. So, fluoropolymer coatings are suitable for lowering the surface energy due to their high content of $-CF_3$ and $-CF_2$ groups [4,22]. There are many methods for surface roughening such as grinding [27–31], sandblasting [32–34], particle coating [22,23,35–45], plasma treatment [2,13,15,46–49], chemical etching [1,19,20,33,34,44,50], lithography [2,11,18,51], electrochemical etching [7,52,53], laser etching [7]. Many approaches of fabricating superamphiphobic surfaces, such as dip coating [1,7,13,15,20,33,52–54], electrochemical dip coating [55–57], casting [14,58], spin coating [2,22,23,39,59] and vapor deposition [7,11,18] have been reported. It should be noted that the large scale commercial application of such fabrication techniques have been very limited because they have special equipment, expensive material, complex process and long period

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[3,4,6,44]. So, there is a need to develop simple and scalable method such as spray coating. There are very few artificial superamphiphobic surfaces that have been fabricated by spray coating [4,6,24,41,58].

In this article, we report the design and fabrication of a superamphiphobic coating on stainless steel surface using spray coating method. Although a few oleophobic and superhydrophobic stainless steel surface have been fabricated [42,44,60,61], it seems that this is the first superamphiphobic surface on stainless steel. Multiscale roughness structure was fabricated by silica particles coating and the particles of upper layer were modified with perfluorodecyltriethoxysilane (PFDTES). The wettability behavior and corrosion resistance of coatings were investigated. Because of the simplicity of the procedure, these coating can be used to coat large areas on a variety of substrates. To the best of our knowledge, this is the first study to investigate the amphiphobicity and corrosion resistance of SiO_2/PFDTES coatings with hierarchical structure on stainless steel surfaces. This work has been accepted as a patent in Iran.

2. Materials and methods

2.1. Materials

1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFDTES) and tetraethoxysilane (TEOS) were purchased from Aldrich. The common chemicals including ethanol, acetone, ammonium hydroxide (25% NH_3 in water) and distilled water were obtained from Merck. All starting materials were used without further purification. Stainless steel wafers with sizes of 2.5 × 3 cm were selected as the substrate.

2.2. Fabrication of superamphiphobic surface

The steel substrates were degreased with acetone and dried in a nitrogen stream. Then, the cleaned surfaces were sandblasted with silica grains and then cleaned with acetone, followed by drying in N_2 gas. After that, the sandblasted plates were coated by silica particles that were produced according to the Stober method. The SiO_2 coating solutions were prepared by mixing TEOS-acetone solution (3 ml in 35 ml acetone) and ammonium hydroxide–acetone solution (certain amount of ammonium hydroxide in 40 ml acetone and 1 ml deionized water). This mixture was added to a three-necked flask equipped with a condenser and magnetically stirred at 60 °C for about 20 h. The particle size of silica was controlled by adjusting the concentration of ammonium hydroxide. It should be mentioned that the particle size increases with increasing the concentration of ammonium hydroxide. Three final mixtures were composed of spherical silica particles which had a mean diameter of about 350 nm (solution A), 160 nm (solution B) and 20 nm (solution C). After that, a fluoro-containing mixture (1.2 ml PFDTES in 100 ml acetone) was fabricated (solution F). The solution F was separately mixed with each of solution B and C, and then magnetically stirred for about 3 h (solutions BF and CF). Each of obtained silica sols was sprayed on the substrates using an air brush atomizer from a distance of approximately 28 cm above the substrate, and then dried at an oven for 75 min (A, B, BF, CF and F films). The temperature of oven was 400 °C for A and B films and 110 °C for F, CF and BF films. The fabricated surfaces and their coatings have been listed in Table 1. Prior to surface characterization, obtained films were rinsed with ethanol and dried in a nitrogen stream.

2.3. Characterization

The distribution of silica particles and their average diameter were measured by dynamic light scattering (DLS). The DLS measurement was performed on a nanoparticle size analyzer (Cordon, France).

Table 1
Coatings and corresponding acronym for each surface.

Coatings	Name
Without coating	R
Sandblasted	SB
Sandblasted and coated with F solution	SB-F
Sandblasted and coated with CF solution	SB-CF
Sandblasted and coated with BF solution	SB-BF
Sandblasted and coated with A, BF solution	SB-A-BF
Sandblasted and coated with A and CF Solutions	SB-A-CF
Sandblasted and coated with A, B and CF solutions	SB-A-B-CF

A field-emission scanning electron microscope (FESEM, Hitachi S4160) equipped with an energy dispersive spectrometer (EDS, Oxford instrument) was used for the structural and elemental analysis of the coatings. Gold-palladium thin film was deposited on the films by a sputter coater (SC7620, England).

The coating thickness was measured according to ASTM B 499 international standard [62] using an elcometer 456 integral coating thickness gauge.

The contact angle was measured by the use of a sessile drop method using a Dataphysics OCA15 Plus contact angle measurement system. The reported CA values are the average of three measurements of CA of droplets at different places on the surface. For each measurement, a 5 ml liquid droplet was dropped on the surface from a distance of 5 cm. The CA was measured when the droplet was in equilibrium state. The deionized water (DI water), ethylene glycol (EG) and fuel oil were used as probe liquids. The sliding angle was determined by tilting the stage and recorded when the liquid droplet started to move.

Potentiodynamic polarization tests were performed using a classical three-electrode setup by scanning the potential at a rate of 9 mV s^{-1}. The corrosion current densities were determined by the Tafel slope technique. The saturated calomel electrode (SCE), platinum grid and unstirred 3.5 wt% NaCl solution were used as reference electrode, counter electrode and electrolyte, respectively. The exposing area of the test sample to the electrolyte was about 5.2 cm^2.

A surface texture measuring instrument (Taylor Hobson, UK) was used to evaluate the surface roughness at nanometer resolution.

In order to evaluate the durability of the prepared films, the samples were immersed in deionized water at ambient temperature for 16 days. After that, the samples were blown dry with N_2 gas, and then the CA of all probe liquids was measured after 0.5, 1, 2, 4, 8 and 16 days of immersion. Also, the CAs and SAs of all probe liquids were measured after the samples had been put in air without special protection for 3 months.

In order to evaluate the hardness of the prepared films, the scratch test performed according to the ASTM G171 – 03(2009)e2 standard [63] using a scratch device made by Parsa Polymer Sharif Company.

3. Theory

The wettability behavior of surface can be interpreted by developed models which were described by Wenzel [64] and by Cassie and Baxter [65]. In the Wenzel model (Fig. 5a), the liquid is in contact with the entire solid surface and completely penetrates into cavities. The Wenzel model states that a rough material has a higher surface area than a smooth one, which modifies the CA according to the expression:

$$\mathrm{Cos}\theta^* = r\mathrm{Cos}\theta \quad (1)$$

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