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Preparation and Corrosion Resistance of 304 Super-hydrophobic Stainless-Steel Surface

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Abstract. Super-hydrophobic stainless-steel surface (SHSSS) was prepared by simple chemical etching method using ferric chloride ethanol solution and nutmeg acid ethanol solution as etching and modification solution respectively. Characterization analyses, including water contact angle (WCA) determination, Fourier-transform infrared spectrometry (FTIR), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and electrochemical workstation were performed on SHSSS.The stainless steel etched with ferric chloride (20 wt%) ethanol solution for 1 h, modified with nutmeg acid, and obtained super-hydrophobic properties (WCA = 151.6 °). Furthermore, the SHSSS has satisfactory chemical stability and corrosion resistance. The surface can maintain super-hydrophobicity within 3.5 wt% NaCl solution of 2 days. The corrosion inhibition efficiency calculated by the fitting parameters of Tafel polarization curve is 81.8%.

1. Introduction

As a common engineering material, stainless steel is widely used in industry, agriculture and our daily life due to its excellent corrosion resistance and mechanical properties. However, corrosion of stainless steel is a very serious problem at present [1]. Thus, enhancing the chemical stability and corrosion resistance of stainless steel has attracted more and more attention. Due to the self-cleaning and waterproof properties of super-hydrophobic surface, the metal surface can be treated into super-hydrophobic surface to delay the occurrence of corrosion [2-3].

Super-hydrophobic surface is a special class of surface with apparent WCA greater than 150 ° and rolling angle less than 10 ° when the water droplets on the surface of the material, such as butterfly wings and rice leaves [4-6]. Modifing low surface energy substance on rough surface and constructing appropriate micro/nano rough structures on the surface of hydrophobic surface are two types of methods to prepare super-hydrophobic surface[7]. At present, the methods of preparing SHSSS include chemical etching [8], laser etching [9], gas-phase deposition [10], electrochemical method [11], and composite coating [12], but most of them are greatly restricted in industry application due to the disadvantages of complex process, high preparation requirements and long preparation period. The chemical etching is etching the solid surface directly with chemical solution to get the appropriate rough structure, and modifying with low surface energy substance later to achieve the super-hydrophobicity. Therefore, chemical etching has the advantages of easy control of roughness, simple equipment and operation.Yu, et al. [8] performed sandblasting processing on X52 pipe steel to obtain micron grade structure, etched with hydrochloric acid solution to obtain nanostructure, then modified with fluorine silane by the surface, and obtained super-hydrophobic surface with micro/nano composite structure (WCA = 156.4 °). Li, et al. [13] etched 304 stainless steel surface with hydrofluoric acid to obtain petaloid microstructure, then deposited fluorine carbon compound thin film on the surface to obtain SHSSS (WCA = 159.9 °).

SHSSS prepared by ecthing with ferric chloride ethanol solution and modifying with nutmeg acid has not be reported. Thus, SHSSS has been prepared by etching with ferric chloride ethanol solution and modifiying with nutmeg acid ethanol solution. Surface morphology, wettability and chemical composition of SHSSS were analyzed, and hydrophobic properties and corrosion resistance of SHSSS were tested in this paper.

2. Experimental

2.1. Main materials

304 stainless steel (Table 1) came form Yangzhou Stainless Steel Co., Ltd. Ferric chloride (≥ 99.0%), Nutmeg acid (≥ 98.0%) and anhydrous ethanol (analytically pure) came from Sinopharm Chemical Reagent Co., Ltd.

Table 1. Chemical composition of 304 stainless steel

C (wt%)	Cr (wt%)	Ni (wt%)	Fe (wt%)
4.11	17.28	6.74	60.74

2.2. preparation of SHSSS

First, the stainless steel surface was cleaned by polishing for 20 minutes with metallographic sandpaper until a polished surface yielded to sweep away oxides, ultrasonic cleaned 3 times using anhydrous ethanol and acetone respectively, each time for 5 minutes, rinsed with deionized water, dried with nitrogen, and the cleaned stainless steel was obtained. Then, the cleaned stainless steel was reacted with ferric chloride ethanol solution (wt% = 20%) for 1h, rinsed 3 times with deionized water, dried with nitrogen, and the etched stainless steel was obtained. Finally, the etched stainless steel was reacted with 10 mM nutmeg acid ethanol solution for 5 h at 60 °C, rinsed 3 times with deionized water, dried with nitrogen, and the modified stainless steel was obtained. The surface of modified stainless steel should be SHSSS.

2.3. Characterization analysis of SHSSS

SEM (XFlash Detector 430-M) was performed to observe the surface morphology of SHSSS. The WCA was determined by contact angle meter (TBU 90E) at room temperature. Deionized water was used as the detection liquid (volume = 5 μL). The average value of 6 points was used as the WCA of the sample. The surface chemical composition of the sample was tested by Fourier-transform infrared spectrometry (Nicolet Nexus 870, reflected mode). The sample surface elements were analyzed qualitatively by SEM energy spectrometer (XFlash Detector 430-M). The corrosion resistances of cleaned stainless steel and SHSSS were determined with Nyquist plots and polarization curves tested by CHI-600 electrochemical workstation (Gamry Co., Ltd, USA).

3. Results and discussion

3.1. Surface morphology and wettability of SHSSS

SEM was uesd to obtain micrographs of SHSSS at 5000 times and 10000 times (Figure 1). Micro bump and groove structure was observed on perpared SHSSS, nutmeg acid deposition particles (< 1 μm) can be obseved in the rough structure, and the deposition particles caused the formation of the micro/nano structure on stainless steel surface. The WCA (151.6°) was of SHSSS was bigger than cleaned stainless steel surface (119.6°) (Figure 2). Water droplet was unstable on SHSSS and quickly dropped with a slightly sloping of surface (< 5 °), suggested a small rolling angle. Thus, the stainless steel surface reached the level of super-hydrophobic. This transformation of surface wettability can be explained by Cassie-Baxter equation. According to the equation, a part of the droplet is direct contact with solid surface protrusions, and the other is contact with air. Thus, the apparent contact angle can be expressed as:

$$\cos\theta = f\cos\theta_w + f - 1 \tag{1}$$

Where, θ_w is the intrinsic contact angle (the WCA of the cleaned stainless steel), θ is the apparent contact angle (the WCA of the SHSSS), and f is the solid and liquid contact area accounts for the percentage of the composite contact area. According to θ = 151.6 °, θ_w = 119.6 °, then f = 0.238 can be obtained, thus, 76.2 % area of the water droplet direct contact with air, only 23.8 % area contact with SHSSS. The microstructure of SHSSS may be suitable for maintaining the air into interspace of the rough structure and forming a layer of air cushion between the droplet and SHSSS [14], as a result, water droplet was effectively prevented to wet the surface, and the contact area between water droplet and the surface was reduced, intuitive performance is the WCA of the surface increasing to 151.6 °.

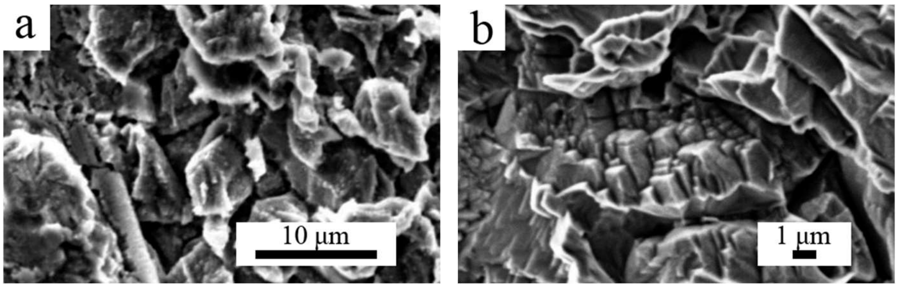

Figure 1. SEM micrographs of SHSSS

(a) 5, 000 times (b) 10, 000 times

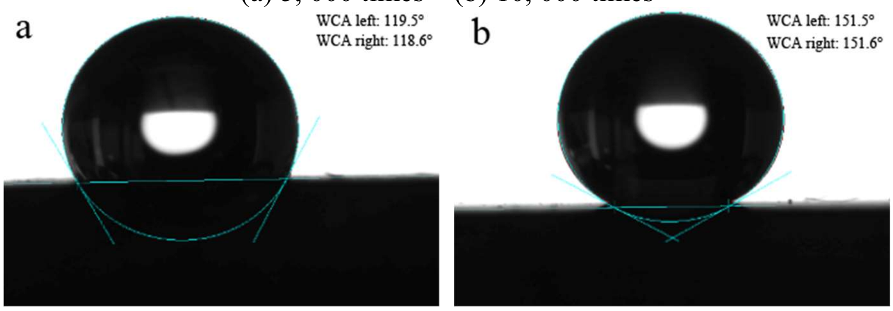

Figure 2. WCA image of cleaned stainless steel surface and SHSSS (a) cleaned stainless steel surface (b) SHSSS

3.2. Chemical composition

Figure. 3 is FTIR spectrum of the surface of super-hydrophobic stainless steel powder. The absorption peaks appear at 2916.6 cm^{-1} and 2848.9 cm^{-1}, respectively attributed to anti-stretching vibration and symmetric stretching vibration of methylene ($–CH_2$) [15], absorption peaks at 1648.8cm^{-1} attributed to anti-stretching vibration of carboxylate ($–COO^-$) [16]. Thus, the Figure. 3 suggested that nutmeg has been adhered to the stainless-steel surface.

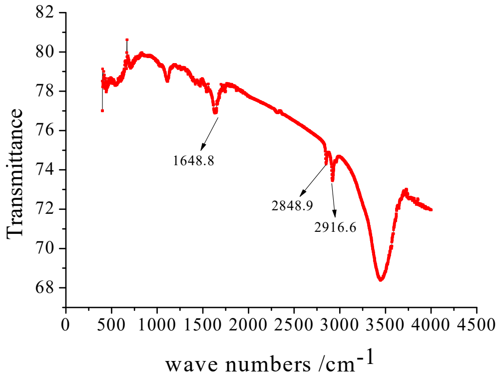

Figure 3. FTIR spectrum of modified stainless-steel powder

EDS analysis was performed on the stainless steel surface to confirm the chemical composition, and the results are shown in Figure 4 and Table 2. According Figure 4(a), C, Fe, Ni and Cr elements were significantly observed on the cleaned stainless steel surface, with the corresponding atomic percentages being 4.11 %, 60.74 %, 6.74 % and 17.28 % respectively. After etching and modifying, Fe content on stainless steel surface was significantly reduced (Figure 4(b)), and its atomic percentage decreased from 60.74% to 48.22%. Thus, the result further indicated the reaction between nutmeg and stainless steel, consisted with FTIR spectrum (Figure 3). In ecthing, Fe in stainless steel reacted with Fe^{3+} in ferric chloride ethanol solution, part of Fe was oxidized into Fe^{2+} and entered solution. In modifying, stainless steel surface was bonded with the hydrophobic long chain of nutmeg acid, and stainless steel surface reached super-hydrophobicity.

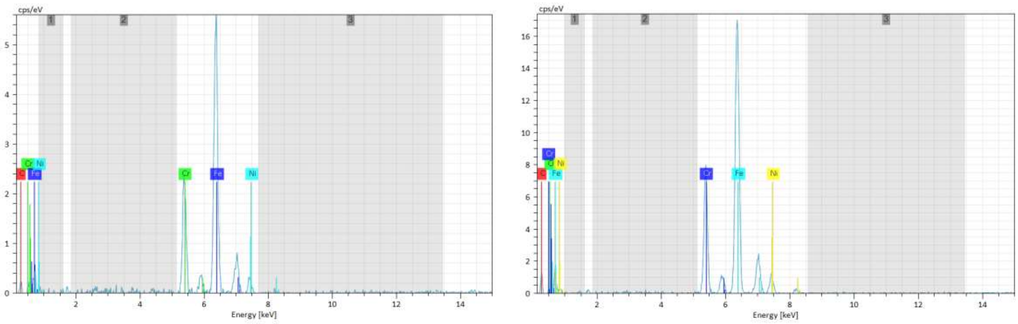

Figure 4. EDS spectrum of cleaned stainless steel surfaces and SHSSS (a) cleaned stainless steel surface (b) SHSSS

Table 2. The atomic percentages of cleaned stainless steel surfaces and SHSSS

	atomic percentages of chemical elements (%)			
	C	Fe	Ni	Cr
cleaned stainless steel surface	4.11	60.74	6.74	17.28
SHSSS	4.08	48.22	6.62	16.82

3.3. Chemical stability and corrosion resistance

In the practical application, chemical stability and corrosion resistance of super-hydrophobic surface are vital. Thus, a series of test was performed on the prepared SHSSS.

The chemical stability can be reflected with the variation range of the WCAs on the surface with the variation of soak time in water and organic solvent [17-19]. The WCA was obtained by the average value in triplicate. Figure 5 shows the change curve of WCAs on the SHSSS with the increase of soak time in water, ethanol and 3.5 wt% NaCl solution. The increasing of soak time in different solution can all decreased the WCAs on the SHSSS gradually. Within the soak time of 2 d, WCAs were about 150 °, and the super-hydrophobicity of SHSSSs were maintained, showed that SHSSS has satisfactory chemical stability in a certain period of soak time. With the increasing of soak time, the WCAs were all continuously decreased, and the super-hydrophobicity gradually lost and changed into the hydrophobicity. The reason may be that the assembled long hydrophobic chain of nutmeg acid on the stainless steel surface disconnected from the surface in water, ethanol and NaCl solution, thus WCAs of on the surface continuously decreased. The longer the soak time was, the more hydrophobic long chain disconnected and the decreasing of WCA was greater.

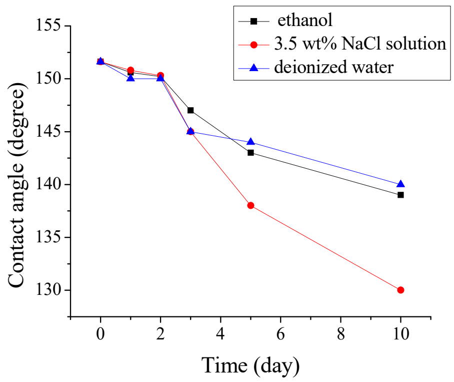

Figure 5. The change curve of WCAs of SHSSS with the increase of soak time in different solutions

The chemical stability also can be reflected with the variation of the WCA on the surface with soaking in a series of solution have different pH (1-14) for 24h [20]. Figure 6 shows the relationship between the WCA of SHSSS and pH (adjusted by hydrochloric acid and sodium hydroxide) of solution. SHSSSs have large WCAs (> 150°) in solutions, except strong acid (pH = 1, 2, 3, 4) or alkali (pH = 12, 13, 14) solution. Thus, the SHSSS can maitain super-hydrophobic properties in a large pH range (5-11) of solutions. However, the SHSSS lost super-hydrophobic properties in strong acid or strong alkaline solution, thus, its application may be districted, and the problem will be study as a new branch in the future.

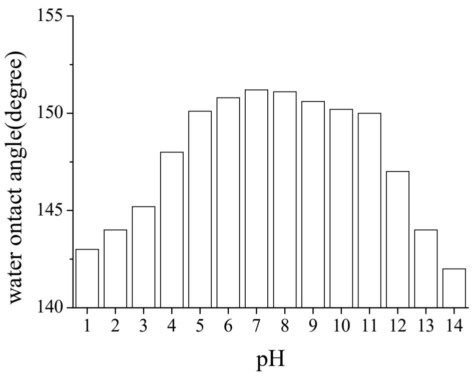

Figure 6. WCA of SHSSS after soaking in solution with different pH for 24h

Tafel polarization curves of cleaned stainless steel surface and SHSSS in 3.5 wt% NaCl solution (Figure 7) were performed by electrochemical workstation to test the corrosion resistance. The fitting parameters, corrosion potential (Ecorr) and corrosion current density (Icorr) was shown in Table 3 according Tafel polarization curves in Figure 7. The Ecorr of SHSSS (-0.221V) was more positive than Ecorr of cleaned stainless steel (-0.302V), and the Icorr of SHSSS (3.471×10^{-6} A·cm^2) was much lower than Icorr of cleaned stainless steel (2.151×10^{-5} A·cm^2). In Tafel polarization curves, more positive Ecorr corresponds to better corrosion resistance, lower Icorr corresponds to slower corrosion rate. The corrosion inhibition efficiency (η) of SHSSS calculated from the fitting parameters is 83.8%. As a result, SHSSS has better corrosion resistance than cleaned stainless steel surface.

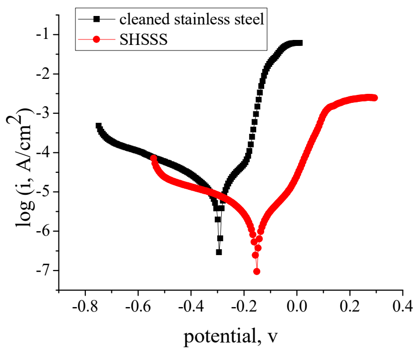

Figure 7. Tafel polarization curves of cleaned stainless steels surface and SHSSS in 3.5 wt% NaCl solution

Table 3. Fitting parameters for Tafel polarization curves of cleaned stainless steel surface and SHSSS

	E_{corr} /V	I_{corr} / A·cm^{-2}	η /%
cleaned stainless steel surface	-0.302	2.151×10^{-5}	
SHSSS	-0.221	3.471×10^{-6}	83.8%

4. Conclusion

Micro bump and groove structure on the cleaned stainless steel surface was obtained by etching with ferric chloride ethanol solution, micro/nano rough structure consisted with nutmeg acid deposition particles was obtained by modifying with nutmeg acid ethanol solution, then SHSSS with satisfactory wettability (WCA = 151.6°) was obtained through this simple chemical etching method.

The hydrophobicity of SHSSS were analyzed using Cassie-Baxter equation, and only 23.8 % area of the water droplet directly contacted solid surface, and the remaining 76.2 % area contacted with air.

The super-hydrophobicity of prepared SHSSS maintained after soaking in water, ethanol and 3.5 wt% NaCl solution of 2 d and different pH (5-11) solution of 24 h, suggested a satisfactory chemical stability. The corrosion inhibition efficiency of SHSSS was 83.8%, suggested a satisfactory corrosion resistance of SHSSS.

Acknowledgments

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References

[1] G Wang, Z Zeng, J Chen, et al. Ultra low water adhesive metal surface for enhanced corrosion protection, Rsc Advances, 6(2016):40641-40649.

[2] L Zhao , Q Liu, R Gao, et al. One-step method for the fabrication of superhydrophobic surface on magnesium alloy and its corrosion protection,antifouling performance, Corrosion Science. 80 (2014) 177-183.
[3] Y Liu, J Liu D, S Y Li, et al. One-step method for fabrication of biomimetic superhydrophobic surface on aluminum alloy, Colloids and Surfaces A. 11 (2015) 125-131.
[4] B.K. Nayak, P.O. Caffrey, C.R. Speak, et al. Superhydrophobic surfaces by replication of micro/nano-structures fabricated by ultrafast-laser-microtexturing, Applied Surface Science. 266 (2013) 27-32.
[5] Y M Zheng, X F Gao, L Jiang. Directional adhesion of superhydrophobic butterflywings, Soft Matter. 3 (2007) 178-182.
[6] K S Liu, X Yao, L Jiang. Recent developments in bio-inspired specialwettability, Chemical Society Reviews. 39 (2010) 3240-3255.
[7] X H Xu, Z Z Zhang, J Yang. Fabrication of Biomimetic Superhydrophobic Surface on Engineering Materials by a Simple Electroless Galvanic Deposition Method, Langmuir the Acs Journal of Surfaces & Colloids. 26 (2010) 3654-3658.
[8] S R Yu, J A Liu, W Diao, et al. Preparation of a bionic microtexture on X52 pipeline steels and its superhydrophobic behavior, Journal of Alloys & Compounds. 585 (2014) 689-695.
[9] B H Luo, P W Shum, Z F Zhou, et al. Preparation of hydrophobic surface on steel by patterning using laser ablation process, Surface & Coatings Technology. 204 (2010) 1180-1185.
[10] K. Nakasa , R Wang, A. Yamamoto. Superhydrophobicity produced by vapor deposition of a hydrophobic layer onto fine protrusions formed by sputter-etching of steels, Surface & Coatings Technology. 210 (2012) 113-121.
[11] J Liang, D Li, D Wang, et al. Preparation of stable superhydrophobic film on stainless steel substrate by a combined approach using electrodeposition and fluorinated modification, Applied Surface Science. 293 (2014) 265-270.
[12] D Yu, J Tian, J Dai, et al. Corrosion resistance of three-layer superhydrophobic composite coating on carbon steel in seawater, Electrochimica Acta. 97 (2013) 409-419.
[13] L Li, V. Breedveld, D.W. Hess. Creation of superhydrophobic stainless steel surfaces by acid treatments and hydrophobic film deposition, Acs Applied Materials & Interfaces. 4 (2012) 4549.
[14] R.N. Wenzel. Resistance of solid surfaces to wetting by water, Ind. eng. chem. 28 (1936) 988-994.
[15] C Zhi, L M Hao, A Q Chen, et al. A rapid one-step process for fabrication of superhydrophobic surface by electrodeposition method, Electrochimica Acta. 59 (2012) 168-171.
[16] I.A. Larmour, G.C. Saunders, S.E.J Bell. compressed metal powders that remain superhydrophobic after abrasion, Acs Applied materials & interfaces. 2(2010) 2703-2706.
[17] T.T. Isimjan, T. Wang, S. Rohani. A novel method to prepare superhydrophobic, UV resistance and anti-corrosion steel surface, Chemical Engineering Journal. 210 (2012) 182-187.
[18] W G Xu, T Ning, X C Yang, et al. Fabrication of superhydrophobic surfaces on zinc substrates, Applied Surface Science. 257 (2011) 4801-4806.
[19] L.B. Boinovich, S.V. Gnedenkov, D.A. Alpysbaeva, et al. Corrosion resistance of composite coatings on low-carbon steel containing hydrophobic and superhydrophobic layers in combination with oxide sublayers, Corrosion Science. 55 (2012) 238-245.
[20] Y Liu, J Liu, S Li, et al. Biomimetic superhydrophobic surface of high adhesion fabricated with micronano binary structure on aluminum alloy, Acs Applied Materials & Interfaces. 5 (2013) 8907-8914.