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Fabrication of lotus-leaf-like superhydrophobic surfaces via Ni-based nano-composite electro-brush plating

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ABSTRACT

Superhydrophobic surface has become a research hot topic in recent years due to its excellent performance and wide application prospect. This paper investigates the method to fabricate superhydrophobic surface on carbon steel substrate via two-layer nano-composite electro-brush plating and subsequent surface modification with low free energy materials. The hydrophobic properties of as-prepared coatings were characterized by a water sliding angle (SA) and a water contact angle (CA) measured by the Surface tension instrument. A Scanning electron microscope was used to analyze the surface structure of plating coatings. Anti-corrosion performance of the superhydrophobic coating was characterized by a potentiodynamic polarization curve measured by the Electrochemical workstation. The research result shows that: the superhydrophobic structure can be successfully prepared by plating nano-C/Ni and nano-Cu/Ni two-layer coating on carbon steel substrate under appropriate technology and has similarity with lotus-leaf-like micro/nano composite structure; the contact angle of the as-prepared superhydrophobic coating can be up to 155.5°, the sliding angle is 5°; the coating has better anti-corrosion performance compared with substrate.

1. Introduction

Superhydrophobic surfaces have wide application prospect in many fields due to their excellent performance, such as Waterproof, self-cleaning, anti-icing, anti-corrosion, etc. [1–7]. The fabrication and application of superhydrophobic surfaces are always the research hot topics. The most well-known superhydrophobic surfaces are lotus leaves, they have excellent water repellency and self-cleaning capability, this is due to their micro/nano scale roughness and the presence of a thin wax film on the leaf surface [8,9]. There are two ways to fabricate superhydrophobic surfaces, one is manufacturing micro/nano scale roughness on the materials having low surface free energy, the other is manufacturing micro/nano scale roughness on the higher surface free energy materials firstly and then modifying the surface by low surface free energy materials [10–13]. For smooth solid material, the contact angle can only be up to 120° even if it has the lowest surface free energy [14,15], so, the building of micro/nano scale roughness is the key to fabricate superhydrophobic surfaces.

So far, there are many methods to fabricate superhydrophobic surfaces on metal substrate, including solution immersion [16], electrochemical deposition [17–19], chemmical etchin [20], anodic oxidation process [21], chemical vapor deposition [2,22] and so on. But all of them have some deficiencies more or less, such as tedious fabrication, high requirements for the equipment, limits to large-scale production, low mechanical strength, which block their practical application. Herein, we present a simple and flexible nano-composite electro-brush plating method to create superhydrophobic surfaces. The electro-brush plating technology is very flexible and efficient, which can deposit different kinds of coatings and prepare large-area coating, the binding force between coating and substrate is strong and the required equipment is portable. Investigating the fabrication of lotus-leaf-like superhydrophobic surfaces via Ni-based nano-composite electro-brush plating and the anti-corrosion performance of the coatings has important significance in the fabrication and practical application of superhydrophobic surfaces.

2. Experiments

2.1. Materials

NaOH, Na_3PO_4, NaCl, $NiCl_2{\cdot}6H_2O$, $Na_3C_6H_5O_7{\cdot}2H_2O$, $H_3C_6H_5O_7$, $(NH_4)_2C_2O_4$, $NiSO_4{\cdot}6H_2O$, CH_3COOH, HCl(30%), $NiSO_4{\cdot}7H_2O$, $NH_3{\cdot}H_2O$(25%–28%), $(NH_4)_3C_6H_5O_7$, CH_3COONH_4, $NaC1_2H_{25}SO_4$, Additive X, Nano-C particles (spherical particle with smooth surface, 35 nm), Nano-Cu particles (spherical particle with smooth surface, 200 nm), Deionized water. All the materials cited above

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Table 1
Electrolytic cleaning solutions.

Chemical composition	Content (g/L)
NaOH	25.0
Na_2CO_3	21.7
Na_3PO_4	50.0
NaCl	2.4

Table 2
No.2 activation solutions.

Chemical composition	Content (g/L)
HCl	25.0
NaCl	140.0

Table 3
No. 3 activation solutions.

Chemical composition	Content (g/L)
$NiCl_2{\cdot}6H_2O$	3.0
$Na_3C_6H_5O_7{\cdot}2H_2O$	142.2
$H_3C_6H_5O_7$	94.2
NaCl	0.1

Table 4
Preplating solutions.

Chemical composition	Content (g/L)
$NiSO_4{\cdot}7H_2O$	400
$NiCl_2{\cdot}6H_2O$	20
CH_3COOH	68
HCl (30%)	20

Table 5
Nano-C/Ni composite plating solutions.

Chemical composition	Content
$NiSO_4{\cdot}6H_2O$	254 g/L
$NH_3{\cdot}H_2O$ (25%–28%)	105 mL/L
$(NH4)_3C_6H_5O_7$	56 g/L
CH_3COONH_4	23 g/L
$CH_3(CH_2)_{10}CH_2OSO_3Na$	0.1 g/L
$C_2H_8N_2O_4{\cdot}H_2O$	0.1 g/L
C nanoparticles	15 g/L

were used for preparing brush electroplating solution. Absolute ethanol and 1H,1H,2H,2H-Perfluorooctyltrimethoxysilane were used for preparing solution to decrease the free energy of plating coatings. All materials were used as received. E355DD carbon steel was used as the substrate and the dimensions of samples are 70 mm × 45 mm × 7 mm.

2.2. Fabrication of the superhydrophobic coating

Preparation process of nano-composite coating is as follows:

Firstly, the E355DD carbon steel substrate was polished to have a surface roughness height value of about 0.80 μm, rinsed with deionized water, degreased in ethanol and dried in a dry box.

The electrolytic cleaning solutions (Table 1), activation solutions (Tables 2 and 3), preplating solutions (Table 4), nano-C/Ni composite plating solutions and nano-Cu/Ni composite plating solutions (Tables 5 and 6) needed for nano-composite electro-brush plating were prepared.

Nano-composite coatings were prepared through co-depositing nano particles and pure Ni by electro-brush plating (EBP) on E355DD carbon steel substrate. The EBP was conducted in the following steps: electrical cleaning → activation → preplating → plating of nano-C/Ni composite coating → plating of nano-Cu/Ni composite coating. After each step, the sample should be rinsed with deionized water. The main parameters are shown in Table 7. After EBP, the sample was ultrasonically rinsed in ethanol for 30 min and dried in a dry box at 60 °C for 60 min.

Table 6
Nano-Cu/Ni composite plating solutions.

Chemical composition	Content
$NiSO_4{\cdot}6H_2O$	254 g/L
$NH_3{\cdot}H_2O$ (25%–28%)	105 mL/L
$(NH_4)_3C_6H_5O_7$	56 g/L
CH_3COONH_4	23 g/L
$CH_3(CH_2)_{10}CH_2OSO_3Na$	0.1 g/L
$C_2H_8N_2O_4{\cdot}H_2O$	0.1 g/L
Cu nanoparticles	5 g/L
Additive X	56 g/L

A micro/nano scale roughness was built on the sample surfaces after EBP, but the surface free energy is too high, in order to obtain the superhydrophobic surface, the sample should be modified by the low free energy materials. So, the simple was immersed into 1H,1H,2H,2H-Perfluorooctyltrimethoxysilane ethanol solution with a concentration of 2 wt.% for about 40 min at 60 °C, then dried in a dry box at 100 °C for 60 min.

2.3. Characterizations

The water contact angle (CA) was measured by the JC2000C-3Surface tension instrument with 5 μL deionized water droplets applied to five different points for each coating. The measurement method of contact angles was angle measurement way. The water slide angle is the slope of the coating surface relative to the horizontal, on which a loose water droplet starts to slide; the SEM images of superhydrophobic coatings were obtained by a Scanning electron microscope (Hitachi Limited; 3-3000N); anti-corrosion ability of the superhydrophobic coating was evaluated by a potentiodynamic polarization curve measured in 3.5 wt.% NaCl aqueous solution by the Electrochemical workstation (C350).

3. Results and discussion

All experiments were carried out at room temperature. The maximum working voltage used for experiment was 15 V, because when the working voltage was too high, the side-effects increased, and the workpiece would be heated seriously, which resulted in the production of lots of water vapor and hydrogen, the mechanical properties of the coating would be decreased seriously.

3.1. Comparison of single-layer coating and the two-layer composite coating

This paper investigates the hydrophobic properties of single-layer coatings which prepared with different kinds of nanoparticles. Measurement shows that after modification with 1H,1H,2H,2H-Perfluorooctyltrimethoxysilane, the contact angle of single-layer nano-C/Ni composite coating can only be up to 126.6°, single-layer nano-Cu/Ni composite coating can only be up to 135.7°, and water droplets are hard to slip from the surface. It is difficult to fabricate superhydrophobic structure via single-layer nano-composite electro-brush plating. Based on the topography of single-layer coatings, two-layer composite coating was studied. The experiment results shows that the superhydrophobic structure can be fabricate on carbon steel substrate via two-layer nano-composite electro-brush plating under appropriate technology, after modification, the contact angle of two-layer coating can be up to 155.5°, the sliding angle is 5°. Fig. 1 shows the SEM images of different kinds of