Fabrication of adhesive superhydrophobic Ni-Cu-P alloy coatings with high mechanical strength by one step electrodeposition

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**HIGHLIGHTS**

- Electrodeposited Ni-Cu-P alloy films possess adhesive superhydrophobic properties.
- The cauliflower-like superhydrophobic surface is account for rose petal structure.
- These coatings show good pH stability and mechanical properties.

**ABSTRACT**

High mechanical strength superhydrophobic Ni-Cu-P alloy coatings with strong adhesion force were one-step galvanostatically electrodeposited onto low alloy steel substrates, from a citrate- and sulphate-based bath. Surface morphologies of as-deposited Ni-Cu-P coatings were investigated by Scanning Electron Microscope (SEM). The chemical composition, structure, mechanical properties and adhesive/hydrophobic properties of coatings were characterized by energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), nano-indenter, and contact angle meter, respectively. Results showed that Ni-Cu-P coatings had cauliflower-like micro-nano structures and exhibited stable hydrophobicity under different pH values and high adhesive properties without any chemical modification. Hardness test results showed that hydrophobic Ni-Cu-P alloy coatings exhibited a high hardness of about 8.5 GPa. The deposition process of coatings was proposed to illustrate the formation of cauliflower-like micro-nano structures. The mechanism of the hydrophobic and high adhesion characteristic of this surface was explained by Cassie impregnating model. This method of fabricating hydrophobic surface has potential in practical applications such as micro-droplet transportation, corrosion protection and nano patterning.

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1. Introduction

In last few years, super-hydrophobic materials with high adhesion force possess not only a large contact angle (greater than 150°), but also a good adhesion with water. It has been a new research focus for the potential applications in liquid transportation, biochemical separation, in situ detection, and localized chemical reaction [1–5], such as micro-fluidic devices [3,6,7] and nano patterning techniques [4]. These phenomena are firstly observed in biological surfaces, such as gecko’s feet [8], rose petal [9], and butterfly wings [10]. The adhesion of different biological surfaces is attributed to different mechanisms. Hereinto, rose petal model is very famous in relevant areas. As we all know, rose petals exhibit...
high adhesion and superhydrophobicity and this phenomenon is explained [9] by the combination of Cassie’s and Wenzel’s mode. Rose petals are composed of microscale grooves and nanoscale folds on grooves, thus water droplets can only penetrate into the microscale grooves but not into the nanoscale folds to form a partial Wenzel state. The application of this adhesive superhydrophobic surface is focused on the transportation of micro liter-sized liquid droplets [3,6,7,11]. Liu et al. [7] fabricated adhesive superhydrophobic polyimide film as “mechanical hand” to snatch micro-liter liquids. Besides the application of micro liter-sized liquid droplets transportation, another practice was tried by Su et al. [4]. They utilized surface’s high adhesive and superhydrophobic properties to fabricate patterning crystal arrays.

According to the models of superhydrophobic surface, some methods are developed to prepare adhesive superhydrophobic materials [3,6,12–20], such as miniemulsion polymerization [6], electrospinning [3], templating methods [12–14], plasma treatments [15] and just the as-deposited film (the film deposited without any further treatment) [16]. However, most of these superhydrophobic adhesive films with micro/nano structure prepared by these methods are organic materials, which can be easily degraded by organisms, light, chemistry or other factors in open circumstance. Further, the lack of strength is also a fatal disadvantage of these films for practical application.

Thus, we try to fabricate high mechanical strength surface with strong adhesive force and excellent superhydrophobic properties. The one-step electrochemical deposition method is used here. Electrodeposition is a traditional method in preparing coatings with different functions for its convenience and low price. By varying the experimental conditions, the surface morphology may change correspondingly. Hu and co-workers [11,21] has prepared superhydrophobic Ni films with micro-nancone morphology by this method. Although recently some kinds of hydrophobic or superhydrophobic films were fabricated through electrodeposition [11,21–23], the investigations on surface’s strength property and adhesive behavior were limited. For example, Hang et al. [21] has prepared super-hydrophobic surfaces with micro-nancone morphologies, but the processes include two steps, and the surface may not possess adhesion property, according to their explanation in the paper.

Up to now, a few researches reported that Ni-matrix coatings can be deposited to be superhydrophobic by controlling the experimental conditions [22–24]. In this paper, we prepared the superhydrophobic Ni-Cu-P coatings with cauliflower-like morphology by electrodeposition. The Cu and P elements were doped into Ni coatings to improve the coatings mechanical strength [25–27] and to induce the formation of cauliflower-like micro-nano structures. This method could overcome the disadvantages on strength and would be more suitable for practical applications.

2. Material and methods

2.1. Coatings preparation

The deposition of superhydrophobic coatings was carried out at the current density of 200 mA/cm² on low alloy steel substrate from electrolytic bath containing 0.125 mol/L NiSO₄ 6H₂O, 0.005 mol/L CuSO₄ 5H₂O, 0.026 mol/L NaH₂PO₄, 0.05 mol/L citric acid, and 0.12 g/L sodium dodecyl sulfate (SDS). And 0.5 mol/L Na₂SO₄ was added to the electrolyte to enhance solution ion strength. The pH
value of electrolyte was adjusted by the aqueous ammonia to 5.5. All of electrolytes were prepared using analytical grade reagents and deionized water. Prior to electrodeposition, substrates were activated in a diluted HCl and subsequently cleaned by water. After each pretreatment, electrodeposition was performed at room temperature (25 °C) in a two-electrode electrochemical cell with a Ni plate as the anode and a steel substrate as the cathode. During deposition, the electrolyte was stirred with a magnetic stirrer. Ni coatings for comparison were deposited at the similar solution with no CuSO4 and NaH2PO2 compounds. The solution used to test the contact angle is prepared by H2SO4 and deionized water. The pH is adjusted by NaOH.

2.2. Surface characterization

Surface morphologies of coatings were examined by scanning electron microscope (SEM, FEI Quanta 250 FEI, US) and energy dispersive spectroscopy (EDS, Oxford instruments X-Max, England) was applied to analyze the elemental composition in the as-deposited coatings. X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (Bruker-AXS: D8 Advance, Germany). Surface contact angle with water was detected by contact angle meter (OCA20, Germany). Water droplets with a volume of 2.0 µL were dropped carefully onto surfaces. All experiments were performed at room temperature. The mechanical properties of the surface were measured by nano indenter (Nano indenter, G200, US).

3. Results and discussion

3.1. Surface morphology and composition analyses

Fig. 1 shows the SEM images of the Ni-Cu-P and Ni samples deposited at a current density of 200 mA/cm². As shown in Fig. 1a, the as-deposited Ni-Cu-P coating exhibits cauliflower-like structure. In contrast, Ni coating (Fig. 1b) prepared at the same experimental condition does not possess this kind structure. And the cauliflower-like hierarchical structure was formed during the electrodeposition process. The EDS result of the Ni-Cu-P coating is shown in Fig. 2. It is revealed that the as-deposited coating is composed of nickel, copper and phosphorus elements. In order to observe the detail of the surface structures, the high magnify image is conducted, as shown in Fig. 1d. Obviously, the cauliflower-like surface is composed of different hierarchical micro/nano-structures which are similar to rose petal structure. The cauliflower-like surface may be attributed to the special growth process of electrodeposits (Brief schematic diagram in Fig. 3). In this system, ion concentration is sufficient to meet the speed of the electrochemical reaction near the cathode. The pure Ni coating can be deposited at the same condition and its surface is smooth, without any feature structure. If Cu element is added into this solution, the deposition of Cu would affect the Ni deposition process, because the reduction potentials of Ni and Cu are quite different. Cu would be prior deposited on the substrate, making the current density not uniform on the unsmooth substrate surface for the polarization effect. The current density would be different at different positions of the cathode. The next Ni deposition will be first occurred on the Cu particles. That is to say, electrochemical reaction is faster at the sharp corners and the deposition would grow faster. In the end, this process results in such cauliflower-like surfaces. On the other hand, at 25 °C Cu2+ can be reduced by NaH2PO2 to produce Cu in the present of Ni2+. If experimental conditions, like current density, changed, the morphology or distance between these cauliflower-like particles would change correspondingly. Coatings with different morphologies do not always show superhydrophobic property.

3.2. Structure characterization

To characterize the crystal structure, coatings are detected by XRD, shown in Fig. 4. Three strong diffraction peaks near the Fcc Ni (ICSD PDF No. 70-1849) diffraction angles of 44°, 51° and 76° correspond to crystal face (1 1 1), (2 0 0), and (2 2 0) respectively. Meanwhile, the position of these peaks move to the low angle direction as the doping of element Cu and P. Atomic size of element Cu is a little larger than that of Ni, but atomic size of element P is smaller. The addition of the two impurity elements results in the spectrum

![Fig. 2. EDS spectrum of the as-deposited Ni-Cu-P coating.](image1)

![Fig. 4. XRD patterns of the as-deposited Ni-Cu-P alloy coating.](image2)

![Fig. 3. Brief schematic diagram of crystal nucleations and coating growth processes.](image3)
peaks’ final position. The peaks near the diffraction angle of 65° and 82° are ascribed to the substrates Fcc Fe (ICSD PDF. 87-0721). These data can clearly illustrate the obtained coatings are Ni-Cu-P alloys.

3.3. Wettability evaluation

The wettability of the alloy coatings is evaluated by contact angle measurement. Fig. 5a depicts that the contact angle of water with the as-deposited coating can be as high as 153.26°. In contrast, the contact angle of water with the pure Ni coating is about 105.48°. Fig. 5b shows the water droplet sliding behavior, which can be determined by the CA hysteresis (the difference between advancing and receding contact angles) on the surface. Experimental results show that the droplet does not slide even when the alloy coating is turned upside down. It is supposed that the van der Waals’s force between the surfaces and water give rise to strong adhesion [14,28]. It can be deduced that the adhesion is mainly caused by the intimate contact of metal surface and water droplets.

Hierarchical micropapillae and nanofolds are known existed on rose petal’s surface. These micro- and nanostructures provide a sufficient roughness for a superhydrophobicity as well as a high adhesive force with water. And surface morphology of alloy coating obtained in the study is similar with that of rose petal [9].

Generally, there are two superhydrophobic states on a rough surface: Wenzel’s state and Cassie’s state. The former represents a wet contact mode of water and rough surface, where water droplet on the surface to form a high contact angle hysteresis. The latter represents a dewet-contact mode and water droplets can roll off easily owing to the low contact angle hysteresis.

Herein, this adhesive superhydrophobic phenomenon could be explained by Cassie’s impregnating model [9] (Fig. 6). According to the theory of the combination of Cassie’s and Wenzel’s mode, vapor pockets are assumed to be trapped underneath the liquid which gives a composite surface. These highly rough cauliflower-like structures allow the water droplet to partially sit on the air pockets.

According to Cassie’s law for surface wettability [29], such micro/nano structures can be regarded as heterogeneous surfaces composed of solid and air. The apparent contact angle \( \theta’ \) of the coating is described by

\[
\cos \theta’ = f_1 \cdot \cos \theta - f_2
\]

where \( f_1 \) is the normalized interfacial area of the micro/nano structures; \( f_2 \) is that of air among the micro/nano structures; \( \theta’ \) is the contact angle of micro/nano structures’ surface; \( \theta \) is that of the smooth surface.

Available air is trapped in spaces between the micro structures to form a cushion at the coating-water interface to prevent the coating from being wetted. This is the reason why Ni-Cu-P coatings with rough surfaces have better hydrophobic characteristic than the smooth one. Also, the adhesion behavior of the surfaces can be explained by the Wenzel’s mode. The Wenzel’s model describes homogenous wetting by the equation

\[
\cos \theta_{\text{w}} = r \cdot \cos \theta_y
\]

where \( \theta_{\text{w}} \) and \( \theta_y \) are the Wenzel contact angle and Young contact angle, respectively and \( r \) is the roughness ratio, defined as the ratio of the true area of surface to its projected area.

As for the details of contact angle hysteresis, Wenzel’s state can induce a high contact angle hysteresis and Cassie’s state with a low contact hysteresis. Grooves of the solid are wetted with liquid. So, herein, the performance of the adhesive superhydrophobic surface can be explained by the combination of the two superhydrophobic states belonging to petal effect - the Cassie’s impregnating wetting state.

Fig. 7 shows the variation of contact angles with pH adjusted by \( \text{H}_2\text{SO}_4 \) solution. Every point is the average of five data. It indicates that the coating can stay stable hydrophobic property at
different pH environment. In low pH solution, the contact angle is slightly lower than that in other pH solutions. This may be due to the dissolution of Ni in the strong acid environment. The effect of nano-structure on the coating’s surface may become weak as the Ni dissolution.

### 3.4. Nanoindentation determination

The mechanical strength of the adhesive superhydrophobic surface is emphasized in this work. Fig. 8 shows the typical load-depth curves performed by a nano-indenter. It is obvious that for the same pressed depth, the Ni-Cu-P coating should be loaded 560 mN force, three times larger than that for the traditional electrodeposited Ni coating (about 180 mN). As seen in Table 1, the hardness and Young’s modulus of Ni-Cu-P coating are 8.5 GPa and 175 GPa respectively, which are larger than those of traditional electrodeposited Ni coating (4.5 GPa and 135 GPa respectively). The excellent mechanical strength of the Ni-Cu-P superhydrophobic coating could be attributed to the doping of Cu and P element, which result in the refinement of Ni crystal grain. These data demonstrate that Ni-Cu-P alloy coatings obtained in this study exhibit high mechanical strength. The excellent mechanical properties of the obtained coatings may be of benefit to the practical application for superhydrophobic/high adhesive technologies.

### 4. Conclusions

In this paper, high adhesive superhydrophobic Ni-Cu-P coatings with strong mechanical strength are prepared by one-step electrochemical deposition. The SEM images show that the surfaces of as-deposited coatings are comprised of small cauliflower-like particles with micro and nano roughness. The contact angle of the surfaces with water can be as high as 153.26° and the surfaces exhibit good adhesive behavior. The nanoindentation data demonstrate that the coatings possess good mechanical strength with a hardness of 8.5 GPa and a modulus of 175 GPa, much higher than those of traditional electrodeposited Ni coatings. The strong mechanical strength Ni-Cu-P coatings with high hydrophobicity and adhesion have numerous potentials for practical applications such as micro-liquid droplet transportation, protective coatings and nano patterning crystal fabrication.

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### References


**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hardness (GPa)</th>
<th>Young’s Modulus(GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Cu-P coating</td>
<td>8.5</td>
<td>175</td>
</tr>
<tr>
<td>Ni coating</td>
<td>4.5</td>
<td>135</td>
</tr>
</tbody>
</table>


