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Etching and heating treatment combined approach for superhydrophobic surface on brass substrates and the consequent corrosion resistance

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ABSTRACT

Designing micro-nano structure is one of promising method to fabricate hydrophobic surfaces. In this paper, we demonstrated a combining etching and heat treatment approach to achieve a superhydrophobic surface on brass. Following by simple modification using stearic acid, the water contact angle on micro-nano structured brass was 153.6°, along which exhibited good and persistent corrosion resistance in 3.5 wt% NaCl aqueous solutions. This method could provide an effective route to fabricate superhydrophobic surface with corrosion resistance and self-cleaning properties for applications in the metal alloys materials.

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1. Introduction

Superhydrophobic, which is the surface with a contact angle greater than 150°, has attracted great attention of researchers [1]. Due to its importance in fundamental research and industrial application [2], these superhydrophobic surfaces can potentially be used in corrosion inhibition [3–6], self-cleaning [7], anti-sticking of snow or ice, oil–water separation, microfluidic devices [8] and many others. Generally, the superhydrophobic surface can be obtained by coating a low energy hydrophobic surface onto a rough structure with special micro-nano structure [9]. It is well-known that the wettability of surface is influenced by surface roughness. Thus the special micro-nano structure would be the key to build superhydrophobic surface, as described by Wenzel [10] and Cassie and Baxter [11]. In recent years, researchers have attempted to design the micro-nano structures *via* various techniques [12,13], such as template methods [13], chemical etching [14], oxidation [15], electrodeposited sol–gel methods [16], and solution-immersion approaches [17]. However, the fabrication methods above somewhat are costly and complicated, therefore, to find a simple, low cost and appropriate method is still challenging towards the superhydrophobic surfaces.

Brass is widely used in chemical and marine industry due to its good thermal and electrical conductivities. However, brass is an active alloy, which does not resist corrosion well [18] and seriously restricts its practical applications in industry. To overcome this drawback, researchers have applied many methods to protect brass [19]. Generally, the traditional corrosion inhibition methods applied to the brass could not achieve good performance in high corrosive seawater and furthermore cause environmental pollutions [20]. As a new corrosion inhibition technology, superhydrophobic has been applied for corrosion inhibition of many metals. Liu et al. [21] used chemical etching method to construct superhydrophobic surface, which greatly improved the corrosion resistance of copper in the seawater. Zhao et al [22] also constructed superhydrophobic surface on magnesium alloy to improve its corrosion resistance. Although the superhydrophobic surfaces can get good corrosion protection in a short time [23], the stability and durability of corrosion resistance still remained a challenging task, as documented in previous reports that some of superhydrophobic surfaces are easily fragile even by the finger contact [24].

In this work, we report a facile and novel method for the fabrication of superhydrophobic surfaces on brass. By combining chemical etching and thermal treatment method, the micro-nano structures on brass surface could be constructed. After this combined methods treatment, the brass surface was further modified with an ethanol solution of stearic acid [25]. Interestingly, it was found that the time of the stearic acid modification to form strong superhydrophobic

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film with flower structure was 10 s. Moreover, this kind of superhydrophobic surface had stable and persistent corrosion resistance in the seawater. In addition, the effect of etching, heating and modification time had been studied in the paper. On the basis of the experiment results, the formation process and corrosion resistance mechanism of superhydrophobic surface are also discussed.

2. Experiment

2.1. Materials

Brass alloy H85 plates (2 mm thick; composition: 84 wt% Cu, 15.5 wt% Zn, 1 wt% Ni) were purchased from Xiangwei Machinery Co., Ltd., China. Ferric chloride, hydrochloric acid and stearic acid were purchased from Shanghai Chemical Reagent Co., Ltd., China. All reagents were of analytical grade and used as received without further purification.

2.2. Specimen preparation

Brass samples (30 mm × 10 mm × 2 mm) and electrodes (10 mm × 10 mm) were polished with different grades of emery paper (1#, 3#, 6#), cleaned ultrasonically with alcohol and deionized water respectively, and dried in air. The cleaned brass and brass electrode were etched with 30 mL aqueous solution of $FeCl_3$ (10 wt%) contained 100 μL HCl (35–37 wt%) at room temperature for about 45 min, and then these samples and electrodes were washed with alcohol and deionized water and dried again. Subsequently, these samples and electrodes were heated in air at 350 °C for 25 min. Finally, the brass surfaces were modified in an ethanol solution of stearic acid at room temperature for a controlled period of time. The obtained samples were washed with alcohol and deionized water, and then dried for pending test.

2.3. Characterization

The surface morphologies and chemical composition of the samples were investigated with a scanning electron microscopy (SEM, SU-1500, Hitachi, Japan), and an X-ray diffraction (XRD, Cu Kα radiation, Bruker, D8 Advance, and Germany). The contact angle (CA) was measured by K100-MK2 Almighty Tension Meter (KRUSS Germany), and the shape of water drops placed on sample surface was tested with a JC2000C1CA system at ambient temperature.

With an electrochemical workstation (CHI 660E, CH Instruments Inc.) equipped with a standard three-electrode system with a Pt electrode as the counter electrode, a calomel electrode (SCE) as the reference electrode and the sample as the working electrode, the electrochemical properties were conducted in 3.5 wt% NaCl aqueous solution at room temperature. The potentiodynamic polarization curves were measured between −0.15 and 0.15 V (*vs* OCP) with the scanning rate of 1 mV/s. The electrochemical impedance spectroscopy (EIS) measurements were conducted in the frequency range from 100 kHz to 0.05 Hz at open circuit potential with amplitude of perturbation voltage 5 mV.

All samples without specification about immersion time are characterized after only 1 day immersion time in 3.5 wt% NaCl aqueous solution.

3. Result and discussion

3.1. Wettability characterization

The wettability of the prepared brass surfaces were characterized by measuring the static contact angle (CA). Fig. 1 shows the static CAs of the brass etched with different time of 15 min, 30 min, 45 min, 60 min and 75 min in the etching solution before they were heated for 45 min and modified with 10% stearic acid for 10 s. The CAs of the surfaces with different etching time were 137.6°, 145.6°, 153.6°, 141.7° and 136.5°, respectively. Obviously, the values of CAs rose to a peak and then reduced, as the etching time increasing. And for 45 min etching one, the CA was at the peak of 153.6°, which indicated that 45 min is the optimal etching time.

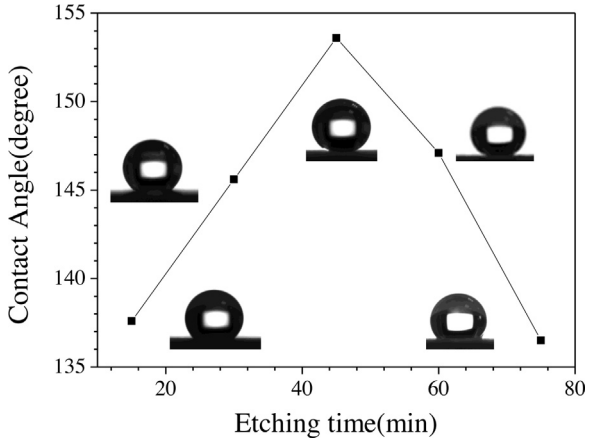

Fig. 1. CA of brass surface with different etching time (15 min, 30 min, 45 min, 60 min and 75 min) in etching solution at room temperature then heat for 20 min and modified with stearic acid for 10 s.

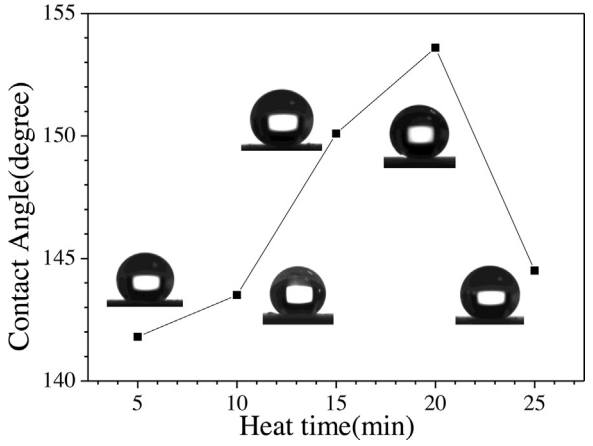

Fig. 2. CA of brass surface treated in the same method with different heat treatment time (5 min, 10 min, 15 min, 20 min and 25 min) at 350°C in the air.

Table 1
Contact angles of brass substrates with the different etched time.

Etched time (min)	15	30	45	60	75
Contact angle (degree)	137.8	145.6	153.6	147.1	136.5

Table 2
Contact angles of brass substrates with the different heat time.

Heat time (min)	5	10	15	20	25
Contact angle (degree)	141.8	143.5	150.1	153.6	144.5

The heating effects were also investigated using 45 min etching sample with different heat time of 5 min, 10 min, 15 min, 20 min, 25 min, at 350 °C. The corresponding CAs were 141.8°, 143.5°, 150.1°, 153.6°, and 144.5° respectively. It could conclude that 20 min was the most appropriate heating time to achieve the best superhydrophobicity.

Taking into account both Figs. 1 and 2, as listed in Tables 1 and 2, it could be seen that the procedure composed of 45 min etching

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