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One-step fabrication of superhydrophobic surface on beryllium copper alloys and corrosion protection application

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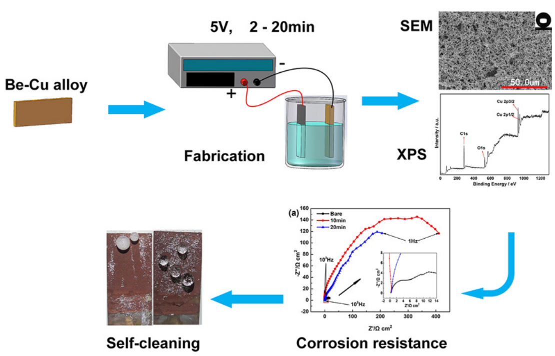
GRAPHICAL ABSTRACT



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ABSTRACT

Superhydrophobic surfaces have a wide application prospect in the future industrial production due to its special abilities. The fabrication of superhydrophobic coating on metal surfaces can improve its performance. A one-step electrodeposition method is proposed to construct nanostructures on the surface of beryllium copper (Be-Cu) alloys, and a mixture of copper chloride and stearic acid is used as the electrolytes. The static contact angle of water on the surface can reach up to 163 ± 4°, a sliding angle of 1.7 ± 0.2°. The nanostructure and chemical composition on the surface were evaluated by scanning electron microscopy and X-ray photoelectron spectroscopy respectively. The corrosion resistance was tested through electrochemical measurement. It was found that the as-prepared superhydrophobic coating improved the corrosion resistance significantly. In addition, the coating with excellent self-cleaning performance was proved. This method solves the problems of complicated process, improves the efficiency effectively, and the electrolyte is eco-friendly.

1. Introduction

At present, the fabrication of superhydrophobic structure on the metal surfaces is a very hot research direction [1,2]. Superhydrophobic surfaces have expansive prospects applying to the industrial production fields due to their special functions, such as self-cleaning, drag reduction, and corrosion protection [3–8]. Performance of equipment in industrial production can be significantly improved by using these properties [9–12]. Through experimental research, it has been found there are two major factors that determine the wettability of the

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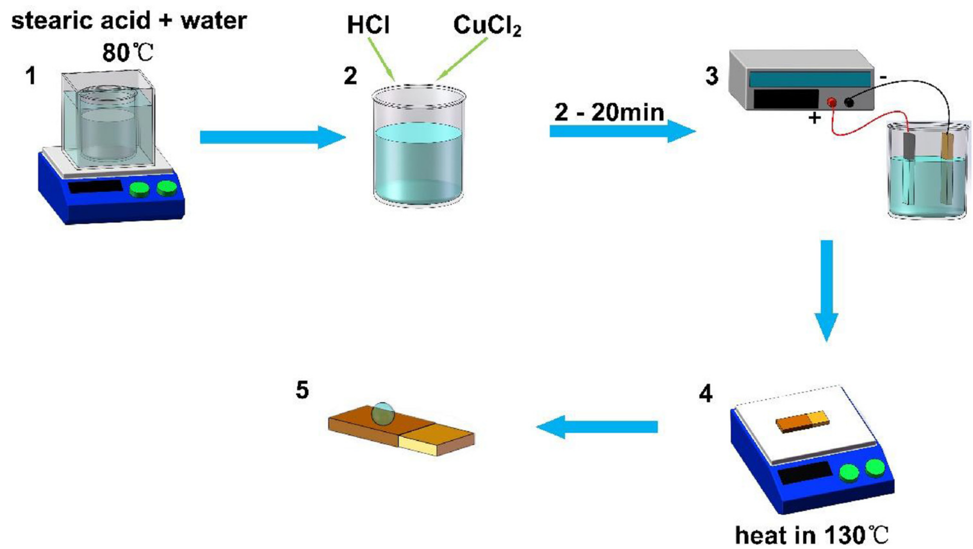

Fig. 1. Schematic illustration of the main operational processes for one-step electrodeposition to fabricate superhydrophobic surface.

surface, they are the rough structure and the surface energy [13–15]. Based on these two factors, we should carry out superhydrophobic surface by fabricating a rough surface with micro-nanostructures and modifying the surface with low surface energy material simultaneously [16–18].

Be-Cu alloy has a very wide range of applications in the fields of aerospace, electromechanical products and communications equipment because of its good wear resistance, good electrical conductivity, good thermal conductivity and anti-interference of electromagnetic [19–21]. Due to the wide application of this alloy material, enhancing its corrosion resistance is very necessary. The superhydrophobic surface has good corrosion resistance [22–24], so to fabricate superhydrophobic coating on the surface of Be-Cu alloy material can improve the performance of the products and enhance the durability of the equipment.

Up to now, there have been many studies on the fabrication of superhydrophobic surfaces by a variety of methods, including electrospinning [25], femtosecond laser technique [26–29], hydrothermal synthesis [30], self-assembly techniques [31], layer-by-layer deposition [17], chemical etching [32], and electrochemical process [33]. These methods are studied on the surface of glass, polymer [10], and metal materials. Chemical etching and electrochemical are the common techniques for fabricating superhydrophobic coating on metal substrates. Chen used a one-step method to etch the surface of the aluminum foils with a mixture of hydrochloric acid and stearic acid for 75 min to fabricate superhydrophobic surfaces [34]; Cui immersed the iron substrates in dilute hydrochloric acid then deposited in platinum chloride, followed by annealing at 170℃ [35]; Liu prepared a mixed solution of cerium nitrate and myristic acid and deposited nanostructures on the surfaces of the magnesium alloy by electrochemical method [36]; Shih-Fu Ou used anodizing on the surface of the NiTi shape memory alloy, and then modified with fluoroalkyl-silane to low the surface energy [37]. Through the previous researches, it has been found that the process of fabricating superhydrophobic surface is complicated, and it is accompanied by the toxicity problem of chemical reagents, moreover the expensive condition of facilities and inefficient process need to be solved.

Here, a non-toxic, non-polluting, one-step electrodeposition method was proposed to fabricate superhydrophobic coating on the surface of Be-Cu alloys. Be-Cu alloy substrates were used as a cathode to deposit copper. The solution mixed cupric chloride, hydrochloric acid, and stearic acid were used as the electrolyte. The method combined the advantages of electrodeposition and low surface energy modification with inexpensive and non-toxic stearic acid at one-step, simple in operation, eliminating the trouble of complicated multi-step process and reducing the risk of mis-operation effectively. The superhydrophobic coating can be changed by electrodeposition parameters adjustment according to different process requirements. The process is easy to control [15,36], and the superhydrophobic coating can be achieved within a few minutes. And its anti-corrosion capacity of the as-prepared superhydrophobic surfaces was evaluated by electrochemical measurement, the results show that the corrosion resistance of the superhydrophobic surface is much higher than the ordinary surface. Broadly applied in aerospace and electronic, the superhydrophobic coating improves the performance of Be-Cu alloy products owe to corrosion resistance enhancement and self-cleaning performance. This method provides an idea for large-scale fabrication of superhydrophobic coating on Be-Cu alloy surface in industrial production due to the efficiency improvement, reducing the mis-operation effectively, simple in equipment low cost and environmentally friendly.

2. Experiment

2.1. Materials and reagents

The Be-Cu alloy sheets (C17200) with the thickness of 2 mm were used as the substrates. The reagents used in the study including copper dichloride ($CuCl_2·6H_2O$), hydrochloric acid (HCl), stearic acid ($CH_3(CH_2)_{16}COOH$), sodium chloride (NaCl), acetone (C_3H_6O), ethanol (C_2H_5OH). All the reagents were analytically pure and used without further purification. Deionized water was used in the whole experiment process.

2.2. Fabrication of superhydrophobic surfaces

Fig. 1 shows the main experimental process. The Be-Cu alloy was cut into sheets with a size of 25 mm × 10 mm × 2 mm. Then the sheets were sequentially polished with silicon carbide paper from 180 to 2000 mesh, ultrasonic pre-cleaned in acetone for 10 min, washed with deionized water, and dried in atmosphere condition. Measuring 60 mg stearic acid into the beaker loaded with 50 ml water, the mixture was dissolved in a water bath at 80℃ for 30 min, 2 ml 0.1 M $CuCl_2$ and 3 ml 1 M HCl were added into the heated mixture, stirred uniformly. Electrodeposition used a DC voltage at room temperature, a Be-Cu alloy sheet as a cathode, a graphite sheet as an anode, a distance between the two electrodes of 15 mm. The operation was carried at a voltage of 5 V for different times (2 min, 5 min, 10 min, 15 min, 20 min), then cleaned