The Effect of Sugar Content for the Wettability of Superhydrophobic Aluminum Substrate

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Abstract. A chemical etching technique is used to prepare a superhydrophobic surface with a honeycomb rough structure on the aluminum surface. Use SEM, Optical contact angle meter and Surface tension detector to characterize the etched aluminum substrate. After the 8th etching, the surface of the sample showed the morphology of micro/nano-scale honeycomb pores and protrusions, and the water contact angle (WCA) is 135°. After being modified with octadecanethiol methanol solution, WCA is 153.1°. After modification, the contact angle of the sample surface decreases with the increase of the glucose solution concentration. When the glucose solution concentration reaches 1000 mg/L, the superhydrophobicity is lost.

Keywords: Aluminum, Superhydrophobicity, Contact Angle, Surface Energy, Sugar Content.

1. Introduction

Wetting is one of the most common phenomena in nature, and wettability is the core issue of many biological processes, engineering and technology [1]. The "lotus effect" is a typical example. With its unique micro-nano structure, it exhibits super-hydrophobicity (contact angle>150°, rolling angle<10°), self-cleaning, and inspired research on bionic wettable surfaces [2]. In recent years, various bionic superhydrophobic materials have been widely used, with representative self-cleaning, anti-icing, oil-water separation, etc. [3-5].

As we all know, the wettability of a solid surface is determined by the surface geometry and chemical composition. Generally, the preparation of superhydrophobic surfaces requires increased roughness and reduced surface energy [6]. Based on this theory, the superhydrophobic surface can be achieved by two methods: (1) processing the rough structure on the surface of low surface energy solid materials (2) modifying the rough structure with low surface energy materials. Methods of preparing hydrophobic surface rough structure: chemical etching, anodic oxidation, laser etching, hydrothermal method, electrochemical deposition, etc.. Commonly used modified materials to reduce surface energy include various organic acids, organic silanes and fluorides, such as stearic acid, lauric acid, perfluoroalkyl silane and octadecyl mercaptan, etc., dissolve them in a suitable solvent in the reaction with the matrix.
In order to make the biomimetic superhydrophobic surface suitable for various industrial fields and our daily lives, it is important to seek simple and feasible preparation methods [7].

The preparation of superhydrophobic surfaces on aluminum substrates by chemical etching and low surface energy material modification is an extremely simple and low-cost method, which has attracted wide attention. On the one hand, due to the crystalline nature of aluminum, the aluminum matrix is not uniform in the chemical reaction, and it is easy to produce micron or even nano-scale rough surfaces. On the other hand, the chemical etching method has the advantages of simple operation, low cost, and short preparation time. B. Yin et al. etched 2024 Al in hydrofluoric acid and HCl solutions, and then surface-modified with fluorosilane (SC-1060F) to obtain a super-hydrophobic surface with a lotus-like papillary structure [8]. Ruijin Liao et al. used CuCl₂, HCl continuous chemical etching and hexadecyltrimethoxy silane surface modification to prepare a micro-nano superhydrophobic aluminum surface [9]. Amani Khaskhoussi et al. used boiling water, HNO₃/HCl etching or HF/HCl etching to achieve surface roughening, and then reduced the surface energy by octadecyltrimethoxysilane (TCODS) to prepare a nano/micro-roughness dual layer structure on the surface of 6082-T6 Al [10].

In this study, a superhydrophobic surface was prepared by combining two roughening methods with low surface energy self-assembled alkyl mercaptans on a 1100 Al substrate. Two pretreatment methods are used: (1) HNO₃ solution etching; (2) zinc immersion. After etching, the Al matrix is dipped and applied to the rough surface by the self-assembled alkyl mercaptan to improve the hydrophobicity of the surface. Using the preparation of super-hydrophobic surface, the relationship between different concentrations of glucose solution and its contact angle was analyzed.

2. Experimental

2.1 Material

The substrate material used in the experiment is 1100 aluminum (Element composition: Si 0.45%, Fe0.35%, 0.05%≤Cu≤0.20%, 0.10%≤Zn, 0.05%≤Mn, Al Balance). Processed into a cube of 10mm×10mm×1.7mm. The chemical reagents used in the experiment ZnO, C₄H₄O₆KNa.4H₂O, C₁₈H₃₈NaO₃S, FeCl₃.6H₂O, HNO₃, NaOH, NaNO₃, NaCO₃, Na₃PO₄ are all analytical pure (China Sinopharm Chemical Reagent Co., Ltd.). Octadecanethiol (C₁₈H₃₈S, 97%, Shanghai Aladdin Biotechnology Co., Ltd., China). All water used is deionized water.
2.2 Preparation of Superhydrophobic Substrate

Use 800#, 1200#, 2000# metallographic sandpaper to polish the surface of the sample to remove surface impurities and oxide layers. After polishing, the sample was ultrasonically cleaned with absolute ethanol and deionized water for 20 minutes, and dried in vacuum for later use. Next, the polished sample was chemically etched. After the 8th etching, the sample was modified in a methanol solution of 0.1 mol/L octadecanethiol for 12h and dried at 120℃ for 120 minutes. The specific process is shown in Figure 1.

The first step is pickling for 60s (HNO₃ solution etching), the second step is zinc immersion for 30s and then pickling for 60s, and then the second step is cycled sequentially. The specific solution composition and process parameters are shown in Table 1. Rinse with deionized water for 2 minutes after each pickling and zinc dipping, and blow dry.

| Type of process | Solution ratio                                                                | t/s | T/℃  |
|-----------------|--------------------------------------------------------------------------------|-----|------|
| Acid pickling   | d=1.42g/cm³, HNO₃(50%)                                                         | 60  | room temperature |
| Zinc immersion  | 50g/L NaOH, 5g/L ZnO, 50g/L C₆H₄O₃KNa.4H₂O, 2g/L FeCl₃.6H₂O, 2g/L NaNO₃, 0.4g/L C₁₈H₂₉NaO₃S (SDBS) | 30  | 25   |

2.3 Characterization

Scanning Electron Microscopy (SEM) (SU3500, JEOL, Japan) was used to characterize the micro morphology of the sample surface with different etching times. Surface tension detector (K-100, Germany) measures the surface tension of glucose solution. Use The optical contact angle meter (DSA-100, Germany) to measure the WCA on the sample surface, randomly select 5 locations on each sample surface (the water droplet volume is 5 uL) for static WCA calculation, and take the average value.

3. Results and Discussion

3.1 Surface Morphology of the Substrate
Figure 2 shows the SEM surface morphology of the sample with different etching times. Figure 2(a) shows the surface morphology of the first etched sample. It can be seen that the surface of the sample is composed of equiaxed grains, and the average grain size is about 0.5-1.8 μm. It can be seen from the map that the matrix is mainly Al phase and trace Si phase. Figure 2(b) shows the surface morphology of the sample etched 8 times. The surface of the sample has a micron-sized honeycomb pore morphology, with a pore size of about 1.1-3.5 μm; the size of the honeycomb hole wall is about 0.2-0.5 μm; the overall structure is micro /Nanocellular rough holes. This morphology may be due to the action of the active agent sodium dodecylbenzene sulfonate (SDBS) added in the zinc immersion solution, which leads to the fine zinc grains deposited, and the fine zinc grains induce the surface grains of the sample after etching small. The ridge in Figure 2(b) is mainly composed of Si element. Because Si has much higher corrosion resistance than zinc and aluminum, the ridge formed by Si element is retained during the short-term etching process. Such micro/nano honeycomb holes provide a good microstructure for the preparation of superhydrophobic surfaces.

3.2 Substrate Wettability

Figure 3 (a) The relationship between the contact angle of the sample surface and the number of etchings; (b) The contact angle of the sample surface
Figure 3(a) is the curve of the relationship between the contact angle of the sample surface and the number of etchings. The water contact angle on the surface of the unetched substrate is 46.1° (Figure 3(b-1)), which shows hydrophilicity due to the inability of the substrate surface to capture air. With the increase of the number of etchings, the water contact angle of the sample surface increases rapidly, and the maximum water contact angle can reach 135.0°. As the number of etchings increases, the water contact angle gradually decreases. It is well known that the surface wettability of samples with hierarchical structure is significantly affected by surface roughness. At the same time, the pits (see Figure 2(b)) are conducive to trapping air, thereby helping to increase the water contact angle of the sample surface. Therefore, as the number of etchings increases, the increase in the water contact angle of the sample surface is due to the combined effect of the surface roughness of the sample and the pit shape. Figure 3(b-3) shows that after the 8th etching, the surface of the sample is modified by n-octadecanethiol, and the WCA increases from 135.0° to 153.1°. This is because the surface of the sample is covered with n-octadecanethiol monomolecular film, thereby reducing the free energy of the sample surface [11].

For solid materials with superhydrophobic hierarchical structure, water droplets usually maintain the Cassie state [12]. The superhydrophobicity shown in Figure 2(b) conforms to the Cassie model. According to the Cassie equation, when water droplets fall on this surface, the air and the solid rough surface form a composite surface [13]:

\[ \cos \theta_C = f_S \cos \theta_S + f_V \cos \theta_V, \]

\( \theta_C \) is the actual contact angle, \( f_S \) is the total area fraction of the contact area between water droplets and solids, \( f_V \) is the total area fraction of the contact area between water droplets and air.

4. The Effect of Sugar Content on the Wettability of the Substrate

![Figure 4](image_url)

**Figure 4.** The relationship curve between the contact angle of glucose solution and the surface tension of the modified sample surface.

Figure 4 is a graph showing the relationship between the surface tension of the sample surface modified with n-octadecanethiol and measuring the contact angle of the glucose solution with different concentrations; and the graph showing the relationship between the surface tension of the glucose solution with different concentrations. It can be seen from the figure that as the glucose concentration increases, the contact angle and the surface energy of the glucose solution both decrease. The concentration of glucose solution is from 110 mg/L to 200 mg/L, the CA is from 152.9° to 151.4°, the surface energy is from 72.41 mN/m to 72.01 mN/m; the concentration of glucose solution is from 200 mg/L to 500 mg/L, the CA is from 151.4° to 150.3°, surface energy from 72.01 mN/m to 62.21 mN/m;
glucose solution concentration from 500 mg/L to 1000 mg/L, CA from 150.3° to 148.7°, surface energy from 62.21 mN/m to 50.25 mN/m. When the concentration of the glucose solution is 1000 mg/L, the matrix loses its superhydrophobic properties. It can be seen from this phenomenon that the modified sample surface with low surface energy has a decreasing contact angle for the glucose solution whose surface energy is gradually decreasing (increased concentration). When the surface energy of the glucose solution is sufficiently low, the superhydrophobicity will be lost. It is conceivable that the method of measuring the contact angle of different human blood (different sugar content) is used to determine whether there is diabetes.

5. Conclusion
A simple, low-cost method that combines chemical etching and surface energy reduction is used to prepare a honeycomb-shaped super-hydrophobic surface on the sample. After 8 times of etching, there are micron-sized holes (1.1-3.5 um) and nano-scale protrusions (0.2-0.5 um) along the edge of the hole on the surface of the sample. The WCA is 135°. The WCA reached 153.1° after modification with octadecanethiol methanol solution. The superhydrophobicity of the Al matrix comes from the combined effect of the surface honeycomb micro/nano structure and the low surface energy modified by n-octathiol. After modification, the contact angle of the sample surface decreases with the increase of the glucose solution concentration. When the glucose solution concentration reaches 1000 mg/L (surface energy 50.25 mN/m), the superhydrophobicity is lost.

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