Properties Investigation and Microstructures Characterization of a Superhydrophobic Coating on 6061Al Alloy Substrate

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Abstract. In this study, a hierarchical structured superhydrophobic coating on 6061Al alloy substrate is prepared through a simple and cheap way using chemical displacement, vacuum heat treatment, and low-energy modification with stearic acid. The coating has the good superhydrophobicity with a static water contact angle (CA) of 158.3 ± 0.2° and a sliding angle (SA) of 5.0 ± 0.2°. The hierarchical microstructures in the Scanning Electron Microscope (SEM) are mainly and randomly distributed micro-particles and feather-like microstructures. Due to these special structures, the Deionized (DI) water has a very low adhesion on the prepared coating. Especially, when the coating was covered with the fly ashes about tens of microns, the ashes are easy to roll off with a 10 μL water drop from the height of 2 cm. Besides, the specimens put in the DI water for 1 months still possess the good superhydrophobicity, the low adhesion and the excellent self-cleaning. When the specimens were taken out of the oven with 200 °C for 12 h, the coating still remains stable in the properties and microstructures. In addition, the specimens put in the outdoor for 10 months still possess the superhydrophobicity with CA of 157.5 ± 0.3° and SA of 6.0 ± 0.2°.

1. Introduction
Aluminium (Al) and its alloys are abundant in nature. Owing to the low-cost and excellent mechanical properties, Aluminium alloys are one of the primary materials used in many engineering and daily life applications [1]. However, the natural protective oxide layer on the surface is easy to be destroyed, especially in the wet and dusty environment. Therefore, the study of protecting Al alloys from the contamination and the corrosion in the service fields is of great realistic significance [2]. Until now, many traditional strategies, such as Cathodic protection, surface oxidization coating, have been widely applied. Unfortunately, there are still some problems while applying these techniques, such as high energy consumption, high cost and the environmental pollution. Actually, it is a big challenge to develop a simple and low-cost approach.

In recent decades, the attempts to take inspirations from nature have affected virtually on every scientific area [3,4]. A novel approach for metal protection has emerged using the extreme wettability, just like the superhydrophobic surface [5-8]. The wettability of solid surfaces is a vital property relating to both the chemical composition and the geometric structure of the surface [9]. Generally, a surface with CA larger than 90° is usually called a hydrophobic surface. When the CA of the solid
surface is larger than 150°, and the SA is less than 10° at the same time, the surface could be called as a superhydrophobic surface [10]. So far, many researches have proved that superhydrophobic surfaces are promising candidates in protecting Al alloys against contamination and corrosion.

Meantime, a great deal of studies indicate that the wettability is mainly dominated by both the morphology of the surface and the chemical composition. Besides, the surface with superior water repellence property is determined by the combination of rough surface with special microstructures and low surface energy materials [9]. Theoretically, the Wenzel state and the Cassie-Baxter state which support a composite solid-liquid-air interface are two potential wetting regimes on rough surfaces that could increase the entrapment of the air in the space between the rough features [6].

Till now, many preparation technologies have been reported for fabricating superhydrophobic surface on Al and its alloys. Yan Liu et al. have fabricated the superhydrophobic film on Al30004 by the laser processing and the surface modification by the dodecyltrimethoxysilane [11]. S. Mokhtari et al. prepared a superhydrophobic surface on Al6061 by the single-step anodizing into anodic aluminium oxide (AAO) and modified by the stearic acid (STA) [1]. Saleema et al. fabricated a superhydrophobic surface on Al6061 by immersing the specimens into the aqueous solution containing sodium hydroxide and fluoroalkyl-silane (FAS-17) [12].

In this study, a superhydrophobic coatings has been fabricated by three steps: the chemical displacement, the vacuum heat treatment, and the low-energy modification on the surface by the stearic acid (STA). The whole process is easy, relatively fast and reproducible. The prepared coating shows the good superhydrophobicity, the low adhesion and the excellent self-cleaning with the good stability of the wettability, even put in the DI water and the outdoor for a period.

2. Experimental procedures

2.1 Materials and reagents

6061Al alloy plates (50 mm × 20 mm × 3 mm) were purchased from Shenzhen Ode Fu Materials Co.Ltd, Guangzhou, China. Anhydrous ethanol, acetone, copper (II) sulfate pentahydrate (CuSO4·5H2O), ferric (III) chloride hexahydrae (FeCl3·6H2O) and the stearic acid (STA) were obtained from Sinopharm Chemical Reagent Co.Ltd, Shanghai, China. They were all analytical reagents. Deionized (DI) water was prepared by an YL-100 water purification system.

2.2 Preparation steps for the coating

In order to remove the natural oxide layer on the substrate, the samples were firstly sanded with sandpapers of 600 #, 1000 # and 1500 # along the horizontal direction and the vertical direction alternately. Prior to the chemical displacement step, the plates were sequentially cleaned by the ultrasonic bath with acetone, ethanol and DI water for 10 min respectively. Then the plates were dried at 80 °C in the oven.

The process of preparing the superhydrophobic coating is as the following steps (as shown in Fig.1). Firstly, the plates were immersed into the 0.40 mol/L CuSO4 and 0.02 mol/L FeCl3 mixed aqueous solution for 60s in the chemical displacement reaction. Then, the plates were thoroughly immersed into DI water to eliminate the residual solution for 10 min and dried at 80 °C in the oven for 20 min. Secondly, the dried plates put in the ceramic boats were heat-treated in a vacuum pipe furnace at 550 °C with the heating rate of 5 °C/min for 2h, and cooled with furnace in 2h. Then the plates were removed from the furnace and set aside. The whole process was on a vacuum condition (<0.1Mpa). Thirdly, the as-prepared 6061Al alloy plates were immersed in 0.02M ethanol solution of the stearic acid at the ambient temperature for 2h and then dried at 80 °C for 30 min. Finally, the superhydrophobic coating was fabricated on the 6061Al alloy substrate.
2.3 Characterizations and tests
The morphologies of the prepared surface were characterized using field emission scanning electron microscope (FESEM, NovaNano SEM 450, FEI). The phase analysis of the surface was performed by X-Ray diffraction (XRD, X’Pert PRO MPD, PANalytical B.V.) with a Cu Kα radiation. The water contact angle (CA) and the sliding angle (SA) measurements were conducted using contact angle goniometer (SL200B, USA, KINO) at room temperature. The roughness of as-prepared sample surface was measured with the Leica DM2500M confocal microscope. For these CA measurements, droplets with a volume of about 3 μL were dropped carefully onto surfaces in the room temperature, and the measurement error of the contact angle is ± 1°. The following data reported was the average of five different positions of the same sample.

3. Experimental results

3.1 Surface Characterizations

3.1.1 The CA and SA measurements of the superhydrophobic coating
The wettability of the sample surface is evaluated by CA. Fig 1.a shows the water CA on the surface of the 6061Al alloy, and the water CA is 76.5°. A polished 6061Al alloy substrate is hydrophilic with the water CA of 41.5° in the Fig 1.b. When the sample was treated after the chemical displacement step, the surface is superhydrophilic (0°) in the Fig 1.c. After above Cu deposits were further processed with the second step of heat treatment, the CA of water was still superhydrophilic (0°) in the Fig 1.d. However, when the above plate was modified by the stearic acid in the low-energy modification step, the water CA on the prepared plates changes from the superhydrophilicity to the superhydrophobicity. The water CA of the coating is 158.3° (error ± 0.2°) in the Fig 1.e. In the first two steps, the sample wettability changes from the hydrophilicity to the superhydrophilicity. Actually, during the chemical displacement reaction, the sample surface is covered with the Cu layer. Besides, the water on the Copper substrate is also hydrophilic, and the water CA is measured about 76.4°.

According to the Wenzel Model, the wettability of the solid surface is related to both the chemical composition and the roughness (r). In our study, the roughness of the polished 6061Al alloy substrate is ca. 0.53 μm. The roughness after the chemical displacement is ca. 9.72 μm. After the second heat treatment step, the roughness is ca. 9.94 μm, which is similar to the first step. In the modification step, the roughness of the superhydrophobic coating is ca. 9.97 μm. The change of the wettability between the polished substrate and the sample treated by the first step is mainly because the surface roughness increases.

It is the amplification effect of r that changes the sample surface from the hydrophilicity to the superhydrophilicity. Besides, the similar state of the wettability between the chemical step and the heat treatment step is also due to the roughness.

However, the wettability of the superhydrophobic surface after the modification being different from those other steps. The main reason is that the chemical composition of the surfaces changes. The stearic acid is a kind substance with a lower surface energy and hydrophobic.
Figure 1. The CAs images of the 6061 Al alloy substrate (a), the polished substrate (b), after the chemical displacement (c), after the heat treatment (d), the superhydrophobic coating (e) and the SA of the superhydrophobic coating (f).

In addition, the SA of the coating was also measured. For the polished plates, the 10 μL water droplet seems to be stuck on the surface, although the tilted angle was above 10°. The plate with only the chemical displacement and the one after first two steps show superhydrophilic, because the water droplets were directly spread on the surface. The water droplet on the superhydrophobic coating is different from the above three surfaces. When the plate is inclined at the degree 5.0° (error ± 1.5°) in the Fig 1.f, the water droplet is easily to roll down. This indicates the prepared coating has a low SA, and its wet state is superhydrophobic.

3.1.2 The morphology and phase on the superhydrophobic coating

In order to find the reason of the superhydrophobicity of the coating. The surface morphology of the coating was studied. For the polished 6061 Al alloy plate, the microstructure is relatively smooth only with some defects, such as scratches and pits in the Fig 2.a. For the superhydrophobic coating, there are the randomly distributed feather-like microstructures and micro-sized particles with various shapes in the Fig 2.b-d.

Figure 2. The SEM images of the polished 6061 Al alloy substrate (a), the superhydrophobic coating (b), the micro-sized particles (c), feather-like microstructures (d).

In the XRD pattern of the polished plate, there are four strong diffraction peaks at 2θ = 38.2°, 43.7°, 64.3° and 77.3° assigned to the Al (111), Al (200), Al (220) and Al (311) planes, which is consistent with the standard powder diffraction peaks of Al in the Fig 3.a. The heat treated plate without the final modified shows that there are also four strong diffraction peaks attributed to the characteristic peaks of the Cu (111), Cu (200), Cu (220) and Cu (311) planes of Cu crystals are detected on the coating at 43.6°, 50.3°, 73.6° and 88.4°, respectively. The above results confirm that the coat deposited on the specimen after the displacement reaction mainly consist of Cu in the Fig 3.b.
Figure 3. The XRD patterns of the polished 6061Al alloy substrate (a), the superhydrophobic coating (b).

Hence, after the plate treated with the first two steps, the surface is covered with the Cu layer, which microstructures are mainly the randomly distributed feather-like microstructures and micro-sized particles with various shapes.

3.2 Property Tests

3.2.1 The Self-Cleaning

Additionally, in order to verify the superhydrophobic coating with the good self-cleaning property like a lotus leaf, the test with the tilt angle of the sample in 8° was shown in Fig 4.a-f. Fly ashes with tens of microns were spilled on the sample. Then, a 10 μL water droplet was dropped onto the sample. The phenomenon is that the fly ashes were washed as the water droplet rolled off. This reason is mainly that the synergy of both the weak adhesion of the fly ashes to the superhydrophobic surface and the high capillary force induced by the water droplet.

Figure 4. The self-cleaning test from a to f.

3.2.2 The Adhesion Test

In the test, the process of the close, the contact and the leave of the water droplet on the coating is shown in Fig 5.a-f. It could be seen that the 5 μL water droplet can easily and completely depart from the coating. This indicates that the water droplet has a low adhesion on the coating. This is partly because the superhydrophobic coating has the complex surface morphology with hierarchical structure and the chemical composition with hydrophobic group that contribute sufficient proportion of the trapped air to the surface and largely increase the repellent force to the water droplet.
3.2.3 The CA and SA measurements after the DI water for 1 month
In order to study the stability of the superhydrophobicity in the DI water for a period of time, the prepared coating was put in the DI water for 1 month. Then, the water CA and SA of the sample were measured compared with the sample before the processing. The result shows that the water CA and SA on the coating after the processing is still stable with the unprocessed samples in the Fig 6.

3.2.4 The CA and SA measurements at 200°C for different times

Besides, the samples were treated at the 200 °C for 3h, 6h, 9h, 12h in the Fig 7. Then, the water CAs of the samples were measured. The result shows that the water CAs of the treated samples are similar to those of the untreated samples. This indicates that the wettability of the samples kept in the oven at 200 °C for 12h are still stable compared with the untreated samples.
4. Conclusions
In this work, the superhydrophobic coating was fabricated on the 6061Al alloy surface by a combined method of chemical displacement, heat treatment and low-energy modification. In addition, the hierarchical structures are made up of randomly distributed feather-like microstructures and micro-sized particles with various shapes. The water CAs of the treated plates without low-energy modification are superhydrophilic. After the low-energy modification, the coating becomes superhydrophobic, and the water SA is about 5.0°. Actually, it is both the morphology and the chemical composition that decide the surface wettability changes of the samples. Besides, the water droplet has the low adhesion. When the samples were kept in DI water for 1 month and at 200 °C for 12h respectively. Compared with the untreated samples, the CAs and SAs of the samples are still stable. Therefore, it can provide a way for protecting the Aluminium and its alloys.

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