Preparation of stable superamphiphobic surfaces on Ti-6Al-4V substrates by one-step anodization

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Superamphiphobic surfaces on titanium alloy substrates were successfully fabricated via one-step anodization and subsequent fluoroalkylsilane modification. The prepared superamphiphobic titanium alloy surfaces display contact angles with water, glycerol and hexadecane are 166.4 ± 1.8°, 158.4 ± 2.1° and 152.5 ± 1.9°, respectively, corresponding sliding angles are all within 10°, which can be attributed to the combination of reentrant micro/nano structures with low surface energy modification. In order to obtain the optimal superamphiphobicity, the relationship between reaction time with wettability of the superamphiphobic surfaces is analyzed in detail. Furthermore, the robustness of the superamphiphobicity is also investigated by UV light test, immersion test and abrasion test, which show that the created superamphiphobic surfaces possess good stability under harsh conditions. The developed approach is simple and has potential to be applied into the commercial production of large-area superamphiphobic titanium alloy surface.

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1. Introduction

Superhydrophobic surfaces display apparent contact angles (CA’s) larger than 150° and small sliding angles (SA’s) with water (surface tension γw = 72 mN/m) [1–3]. These surfaces have aroused extensive interests because of their important uses in self-cleaning, antifogging, and anticorrosion [4,5]. However, conventional superhydrophobic surfaces may be not repellent to organic liquids with very low surface tensions (γL). Superamphiphobic surfaces repel both water and oil extremely, exhibiting CAs above 150° for water as well as various oils [6]. And they may have more wide potential applications than superhydrophobic surfaces, such as water–oil repellent fabrics, crude oil transfer, antifouling and especially oil pollution minimization [7–9]. Therefore, it would be extremely desirable to develop facile methods to create superamphiphobic surfaces on various substrates.

Previously, some researchers have successfully prepared superhydrophobic surfaces on metal substrates by generating hierarchical micro/nanometer-scale rough structures and subsequent low surface energy modification [10–12]. However, creating superamphiphobic surfaces has proven to be much more difficult than creating superhydrophobic surfaces, because specific rough structures, such as overhang or re-entrant structure, are essential to the fabrication of superamphiphobic surfaces [13,14]. To date, some different methods, including chemical etching [15], sol–gel process [16], surface coating [17,18], spray and laser etching [19,20], have been proposed to fabricate superamphiphobic surfaces with hierarchical micro-nano structures. These methods undoubtedly provide feasible solutions on the fabrication of superamphiphobic surfaces on metal substrates. However, they are subject to certain limitations such as the poor controlling performance, tedious processes, low efficiency and high cost. Comparing to those methods, the electrochemical technique is known to have the distinct advantages of good controllability, process simplicity and low cost. So superamphiphobic surface preparation via electrochemical treatment has attracted considerable scientific attention [21,22]. Nevertheless, there are only a few reports that electrochemical techniques have been employed to prepare superamphiphobic surfaces on titanium and its alloy, despite that titanium alloy has very important applications in aviation, shipbuilding and defense industries for its good heat resistance, corrosion resistance as well as high specific strength [23].

For instance, Wang et al. fabricated superamphiphobic titanium surfaces via electrochemical etching in NaCl solution for 1 h and subsequent anodization in an electrolyte containing ethylene glycol, 3% hydrofluoric acid (HF) and 0.5 wt% NH₄F for 1 h [24]. Barthwal et al. also realized superamphiphobicity on titanium substrate by two-step anodization [25]. Lu et al. reported the
preparation of superamphiphobic titanium surfaces through controlling parameters of electrochemical etching in NaBr solution [26]. The above approaches provide a strong basis for fabricating superamphiphobic titanium alloy surfaces. However, they can be improved in the aspects of two-step electrochemical treatment, environmentally harmful reagent and strict reaction conditions. In addition, the stability of the prepared superamphiphobic surfaces also should be given more attention. Lacking for stability under harsh conditions is a common problem for most of the prepared superamphiphobic surfaces, which limits their use in practical applications [27]. Therefore, preparing robust superamphiphobic titanium alloy surfaces is significant.

In this paper, inspired by the existing methods of anodization on titanium [28], we develop a simple, efficient and environment-friendly approach to fabricate superamphiphobic titanium alloy surfaces, which only use one-step anodization to generate hierarchical micro/nanometer-scale structures on titanium alloy surface and then lower the surface energy with the fluoroalkylsilane modification. The superamphiphobic titanium alloy surfaces show apparent CAAs larger than 150° and low SAs, even with liquids possessing a significantly low surface tension, such as hexadecane (γSV = 27.5 mN/m). Moreover, the prepared superamphiphobic surface possesses good stability tested by UV light test, immersion test and abrasion test. This study is expected to create a new avenue for extending the life span of superamphiphobic titanium alloy surfaces and advance the applications of superamphiphobicity.

2. Experimental

2.1. Preparation of superamphiphobic Ti alloy surfaces

Firstly, Ti-6AI-4V substrates (30 mm × 20 mm × 3 mm) were polished with #1200 metallographic abrasive paper and then ultrasonically cleaned in acetone, alcohol and deionized water for 3 min, respectively. After that, they were dried completely with flowing N2 for the subsequent anodization. Secondly, the preprocessed specimens were used as the anode, whereas a graphite plate in the same size as the Ti-6AI-4V specimen served as the cathode. The electrolyte comprised 50/50 volume percent glycerol–water mixture containing 0.3 M NaCl. The anodization was performed under magnetic stirring from 10 min to 60 min at a DC voltage of 30 V. After the above electrochemical process, the titanium alloy specimens were ultrasonically rinsed with deionized water and then dried thoroughly. Lastly, the oxidized specimens were immersed in a 1.0 wt% FAS (tridecafluorooctyltriethoxysilane, C13F27(OCH2CH3)3, Degussa Co., Germany) in ethanol for 2 h and then maintained at 120 °C for 15 min. All experiments were carried out at room temperature.

2.2. Characterization

The micro-morphologies of superamphiphobic surfaces on titanium alloy substrates were observed through a scanning electron microscopy (SEM, JSM-6360LV, Japan), the attached energy-dispersive spectroscopy (EDS, INCA Energy, Oxford135InSs), Fourier-transform infrared spectrophotometer (FTIR, JACSCO, Japan) and the X-ray diffractometer system (XRD6000, Japan) was performed to investigate corresponding surface chemical compositions. To evaluate the surface wettability, CAs and SAs were measured by the sessile-drop method using an optical contact angle meter (DSA100, Krüss, Germany) at room temperature. Liquid droplets (5 μL) were randomly dropped onto the surfaces of the specimens, and the average of five measurements obtained at different positions on the specimens was employed as the final CA. The SA was the angle at which the liquid drop (5 μL) started to roll off the gradually tilted surface. Deionized water, glycerol and hexadecane were adopted for liquid CA and SA tests and dispensed via a micro syringe.

2.3. Surface robustness test

Stability is the foundation of the potential applications for the superamphiphobic surfaces. In this study, UV/corrosion/abrasion resistances for the fabricated superamphiphobic titanium alloy surfaces were tested sufficiently. To evaluate the UV resistance, the CAs of the superamphiphobic surfaces exposed to UV irradiation for 30 days were measured. We also immersed the prepared specimens into acidic or alkaline solution for 30 days to evaluate the corrosion resistance. In the abrasion test, superamphiphobic surfaces to be tested were faced with the 800# SiC sandpaper. Simultaneously, a pressure (2000 Pa) was applied on the superamphiphobic surfaces, and then the surfaces were driven to move 10 cm on the sand paper longitudinally and transversely, which was defined as an abrasion cycle [8]. The CAs were measured after each test.

3. Results and discussion

3.1. Surface morphology

Fig. 1 shows the SEM images of Ti alloy surfaces before and after electrochemical treatment. It is obvious that only some scratches and crevices are on the mechanically polished titanium alloy surface (Fig. 1a–c). After low surface energy modification, this surface is still far from superhydrophobic and superoleophobic, due to lack of hierarchical micro/nanometer structures. Fig. 1d and e show the surface morphologies of the anodized specimen at 5000× and 20,000× magnifications respectively. It can be seen that the surface is covered with pores and protrusions randomly and densely, with sizes in the range of 1–3 μm (Fig. 1d). SEM image at a higher magnification exhibits that nano sized features were generated on the micro sized hierarchical protrusions as shown in Fig. 1e. Importantly, the superimposition of pores and protrusions contribute to the re-entrant structures (Fig. 1f), which can trap a large fraction of air. According to recent study, specific rough structures like the overhang or re-entrant structure are necessary to the formation of a composite solid–liquid–air interface with oil liquids, and when oil droplets are placed on these structures, the Laplace pressure force is directed upward, which can effectively prevent the oils from penetrating into the textures [29]. After FAS modification, the anodized surfaces display superamphiphobic properties, and water, glycerol and hexadecane liquids (5 μL) exhibit typical spherical shapes on these surfaces and easily roll off with the sliding angle all lower than 10° (Fig. 1f). Fig. 1g and h show the SEM images of the anodized specimen surface modified by FAS. It can be seen that there is no obvious morphological difference between specimens with and without being modified by FAS, indicating that the FAS modification has no obvious effect on the reentrant micro/nanometer-scale structures of the prepared superamphiphobic surface.

3.2. Surface chemical composition

To further study the relationship between surface chemical compositions and the superamphiphobicity, EDS and FTIR are used to analyze the chemical compositions of specimen surfaces. Besides, the crystal structures of specimen surfaces are also investigated by XRD. Fig. 2 shows the XRD patterns of the polished Ti alloy surface and the specimen surface anodized for 40 min. It can be observed that both surfaces show some characteristic peaks which are attributed to the formation of TiO2/TiO2O7/TO/Al2O3/VO2/V6O11, indicating that same oxidations have been produced on both surfaces. This can be confirmed by the
fact that the element of O is found on both surfaces (Fig. 3a and b), however the mass fraction of O on the polished titanium alloy surface is lower. It means that general titanium alloy surfaces can also be oxidized in air and only small amounts of oxidations are present on the surface. Before low surface energy modification, the polished specimen surface which exhibits hydrophilicity and oleophilicity becomes superamphiphilic after anodization, which can be explained by Wenzel’s theory that the micro/nano meterscale rough structures have potential to enhance the hydrophilicity/oleophilicity of given hydrophilic/oleophilic surfaces [30]. After FAS modification, some other elements C, F and Si appear on the anodized surface, which then repel water and oil extremely (Fig. 3c). It indicates that FAS molecules maybe have been self-assembled or adsorbed onto the titanium alloy surface.

Fig. 4 shows the FTIR spectrum of the anodized titanium alloy surfaces after FAS modification. The three absorption bands at around $1114$, $1240$ and $1374 \text{ cm}^{-1}$ were attributed to the C=F stretching vibration of the $=\text{CF}_2$— and $=\text{CF}_3$ groups of the FAS molecules. The absorption band at $1052 \text{ cm}^{-1}$ was identified as the framework vibration of $\text{Si—O—Si}$ bonds. The FTIR results further confirm that there is a FAS film on the titanium alloy surface with low surface energy modification. The FAS film has a very low surface.
energy and can effectively reduce the anodized titanium alloy surface energy, thereby contributing to the surface wettability change from superamphiphilicity to superamphiphobicity. Therefore, we can draw conclusion that the combination of the hierarchical rough structures and low surface energy material modification is responsible for the superamphiphobicity of the titanium alloy surfaces.

3.3. Effect of processing time on superamphiphobicity

We studied the effect of processing time by performing a series of experiments at different reaction time with 0.3 M NaCl in the 50/50 volume percent glycerol–water solution and 30 V of DC voltages. Fig. 5(a) and (b) show the changes in the CAs and SAs as the function of reaction time, using water, glycerol and hexadecane as the probing liquids. It is obvious that the specimen surfaces display superhydrophobic and moderate oleophobic to glycerol and hexadecane after 20 min of anodization. The water and oil repellency increased with the reaction time extending within 40 min attributing to that the reentrant micronanorough structures developed gradually on the surface as time went on. Good superamphiphobicity was obtained on the anodized surfaces at 40 min. The CAs for water, glycerol and hexadecane are 166.4° ± 1.8°, 158.4° ± 2.1° and 152.5° ± 1.9° respectively, corresponding SAs are all within 10°. When the reaction time...
Fig. 8. CAs of the superamphiphobic surfaces immersed into the solution with different pH values for 30 days.

Fig. 9. Schematic illustration of the abrasion test performed to evaluate the mechanical robustness of the superamphiphobic surfaces.

go beyond 40 min, the processing time has little effect on the wettability of the specimen surfaces, owing to the relatively stable binary micro-nano rough structures have been generated on the surfaces. It can be confirmed by the surface structures fabricated after a series of reaction time 50 min and 60 min, since the micro/nano rough structures do not show obvious changes (Fig. 6).

3.4. Stability analysis

To investigate the robustness of the superamphiphobic titanium alloy surfaces under harsh conditions, stability tests were carried out. Fig. 7 shows that the CAs slightly change even though the prepared superamphiphobic surfaces have been irradiated with UV light for many days, indicating that both surface morphology and chemistry does not change greatly after UV irradiation. Titanium alloys are very important engineered materials in many industry fields, such as navigation, pipeline transport and biomedical devices. So if the prepared surfaces possess good corrosive resistance, it will have great significance to promote the applications of the superamphiphobic Ti-6Al-4V surfaces. To evaluate the corrosion resistance, we immersed the specimens into acidic or alkaline solution for 30 days to observe their change in wettability for water and oil. Fig. 8 shows the variation of CAs with pH values ranging from 1 to 14 respectively. Minor changes were evident in the CAs, owing to that the hierarchical structures were not etched during the immersion and the FAS layer had a high chemical stability. This suggests that the titanium alloy surfaces are able to retain good amphiphobic stability in corrosive solutions.

Fig. 10. CAs of the superamphiphobic titanium alloy surfaces after circles of abrasion tests.

Fig. 11. Images of 5 µL different liquid droplets on the superamphiphobic titanium alloy surface after abrasion (a) 5 cycles, (b) 10 cycles, (c) 15 cycles and (d) 20 cycles.
We next conducted the abrasion tests to fully study the mechanical robustness of the superamphiphobic surface (Fig. 9). The variation in the values of CAs for different liquid droplets on the structured surface with abrasion cycles is shown in Fig. 10. It can be seen that CAs for both water and oil changed slightly within 10 cycles and liquid droplets all displayed approximately spherical shape on the abraded surfaces (Fig. 11). Implying that the prepared surface still remain high amphiphobicity after being scratched repeatedly. However, the CAs of oil droplets decreased more quickly than water droplets’ beyond 10 cycles due to that binary micro-nano rough structures were damaged constantly during abrasion and the superoleophobicity of titanium alloy surfaces more depended on the re-entrant hierarchical structures. Even so, water, glycerol and hexadecane droplets could easily roll off by a small sliding angle after being abraded repeatedly. It means that the created superamphiphobic titanium alloy surfaces possess good mechanical stability and can withstand practical applications.

4. Conclusion

We proposed a simple, efficient and environment-friendly method to fabricate superamphiphobic surfaces on titanium alloy substrates. The re-entrant micro/nano structures were generated on the specimen surfaces via one-step electrochemical treatment in the electrolyte containing 0.3 M NaCl and 50/50 volume percent glycerol–water mixture. Followed with FAS modification, the as-prepared surfaces showed good superamphiphobicity. The average CAs for water, glycerol and hexadecane are 166.4 ± 1.8°, 158.4 ± 2.1° and 152.5 ± 1.9° respectively, corresponding SAs are all within 10°. Stability tests further proved that the created superamphiphobic Ti-6Al-4V surfaces possess UV/corrosion/abrasion resistances, implying that the obtained surfaces have good chemical and mechanical stability. Hence, we believe that this study could provide a straightforward and effective route to fabricate robust and large-area superamphiphobic titanium alloy surface for a great number of commercial applications.

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