

Femtosecond Laser Fabrication and Chemical Coating of Anti-Corrosion Ethylene-Glycol Repellent Aluminum Surfaces

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Abstract: Ethylene glycol (EG) is widely used as a cooling agent in factories, aviation, and automobiles. However, its corrosive nature can create significant damage and reduce the life cycle of devices. This paper compares three different methods to achieve the superhydrophobic anti-corrosion aluminum surfaces for working in an engine coolant environment. The methods are combinations between femtosecond laser fabrication and chemical coatings using Polydimethylsiloxane (PDMS) and Triethoxy-1H,1H,2H,2H-tridecafluoro-n-octylsilane (TTFOS). All the samples show superhydrophobicity with contact angles greater than 150°, and sliding angles smaller than 10°. The superhydrophobic surface (SHS) show the best corrosion rate up to three orders of magnitude compared to flat surfaces when working in an engine coolant environment. Moreover, corrosion inhibition efficiencies of the fabricated surfaces impress the best results greater than 98%. The anti-corrosion behavior of the SHS is explained. After comparing the performances of the surfaces fabricated by three methods, the most suitable method is proposed to produce anti-corrosion aluminum surfaces for applications using engine coolant as an environment.

Keywords: Corrosion; Ethylene glycol; Laser processing;

1. Introduction

EG has been applied as a refrigerant in many fields like automobiles [1]. For automotive applications, the cooling agent has been used to transfer heat to prevent car engine malfunction. In an automobile's cooling system, a 1:1 dilution of mixture between EG and water is commonly used. However, the -OH group in EG is not stable, which will oxide or degrade to become different acid types. Therefore, the formed acids in the EG solution will cause corrosion problems and reduce the machine's lifetime as time goes on. Corrosion inhibitors are usually added to the coolant solution to prevent acid formation. However, the coolant solution still needs to be frequently changed because it can become more acidic over time and lose its rust-inhibiting properties, causing corrosion on automobile radiators. To reduce the number of changing coolant solutions and protect metal surfaces in the cooling system of automobile radiators, superhydrophobic anti-corrosion metal surfaces can be a good option.

Recently, researches on SHS have become one of the hottest topics due to potential applications for self-cleaning [2]; oil-water separation [3], and anti-corrosion [4]. To our knowledge, there is no work studying the corrosion performance of such surfaces in coolant solutions. Among the methods to get SHS, the femtosecond laser ablation has attracted many researchers' interest for its high efficiency, simple process, and lower cost [5,6] and is widely used in producing the superhydrophobic anti-corrosion surface [7].

This paper uses three methods to produce superhydrophobic anti-corrosion aluminum surfaces by femtosecond laser ablation and chemical coatings. All the samples show excellent superhydrophobicity and anti-corrosion properties with EG solution. Moreover, we made comparisons of the samples prepared by the three methods to suggest the most suitable one for the production of surfaces working in engine coolant environments which brings a possibility to apply EG repellent metal surfaces in the cooling system of automobile radiators for more prolonged usage, resulting in cost-saving and sustainability development.

2. Experimental

2.1. Material

PDMS (Sylgard®184, Dow Corning CO., Michigan), 99.999% pure Al substrate (Zhong Nuo Advanced Material Technology Co., Ltd), TTFOs (Shanghai yuanye Bio-Technology Co., Ltd), and fumed silica (Hydrophobic-260, 7-40nm, Aladdin biochemical technology co. LTD) were used in this research.

2.2. Fabrication

A Al plate ($10 \times 10 \text{ cm}^2$) was divided into smaller pieces with different dimensions ($1.5 \times 1.5 \text{ cm}^2$, $2 \times 2 \text{ cm}^2$). Then, these pieces were ultrasonically cleaned with deionized water (DI water) and ethanol for 15 minutes, respectively, to remove the impurities.

Micro-nano structures on the substrate were fabricated by a femtosecond laser (Fig. 1a). The distance between the ablating lines was $100 \mu\text{m}$, and the scanning speed was $1 \text{ mm} \cdot \text{s}^{-1}$. The fabricated structure is a grid pattern.

The three methods are described below (Fig. 1b):

- Method 1 (M1): Al was fabricated by 200 mW of femtosecond laser power. Then, the PDMS and curing agent (weight ratio of 10:1) were dissolved in the toluene (5 wt.%). Then, we coated the solution on the surface and heated the sample for 1 hour at 150°C .
- Method 2 (M2): The PDMS and curing agent were mixed (weight ratio of 10:1) and then coated on Al substrate. Then, the sample was put on the table for 10 minutes and then heated for 1 hour at 150°C , followed by a femtosecond laser ablation (35 mW).
- Method 3 (M3): A femtosecond laser (200 mW) produces micro-nano structures on the Al. Then, we prepared the synthesized solution, which referred to Jia Hu. et al group [8]. The preparation process was as follows: at room temperature, 0.1 g TTFOs was added to 9.9 g ethanol and stirred for 2 hours to make the TTFOs dissolve utterly, then 0.02 g SiO_2 was added, and after 2 hours of stirring, 1 g PDMS was added and stirred for 1 hour. Finally, a 0.1 g curing agent was added and stirred for 15 minutes to make the solution

thoroughly mixed. After coating this solution, the sample was heated for 5 minutes at 160 °C.

2.3. Characterization

The surface morphology and the element composition were characterized by a scanning electron microscope (SEM) (ProX800-07334, Phenom World), an energy dispersive spectrometer (EDS). The samples' wettabilities were tested by a contact angle measurement machine (powereach JC2000D3). The anti-corrosion properties were tested by the electrochemistry method (EC-Lab, VMP 3) with a 50 vol.% EG solution. After the corrosion test, the sample was dried and then retested by the 3D confocal microscope (KEYENCE VK-X 1000) to see the surface morphology change.

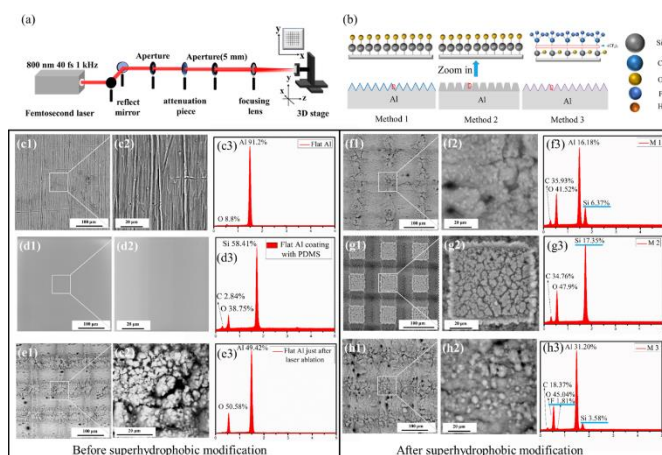


Fig. 1. (a) femtosecond laser system; (b) the chemical coatings on the substrates; (c-h) surface morphologies and element compositions of the samples.

3. Result and Discussion

Fig. 1c-h shows morphologies of the surfaces before and after superhydrophobic modifications. In M1 and M3, significant microgrid patterns did not change much after chemical modification. However, when zooming in on structures at higher magnifications, they were smoother with more nanoparticles' appearance and the disappearance of micro-nano cavities. (Fig. 1e,f,h). The surfaces in M2 contained cube shapes with cracks on the top, significantly differing from the samples prepared by M1 and M3 (Fig. 1g). Moreover, Si and F

appearances indicated chemically modified coatings on the samples of these three methods.

In Fig. 2a, all the fabricated samples showed excellent liquid repellency with the contact angles (CAs) greater than 150° and sliding angles (SAs) smaller than 10° (Table S1 and Fig. S1). Without the micro-nano structure, flat surfaces only with the chemical treatment cannot become superhydrophobic (Fig. 2b). After laser ablation, the contact area between the droplet and the substrate had an about 10-fold decrease (Table S2), which played an important role in improving hydrophobicity. According to the Cassie-Baxter model [9,10], the air layer formed on the surface prevented the droplet from penetrating the structure (Fig. S2). Also, the hydrophobic molecules attached to the surface formed a protective layer in M1 and M3, reducing the surface energy and enhancing hydrophobicity. The laser processing part was mainly cured PDMS layer in M2, while the Al substrate was not exposed, and the PDMS coating was in effect. PDMS had low surface energy, and the rough structure enhanced the sample hydrophobicity.

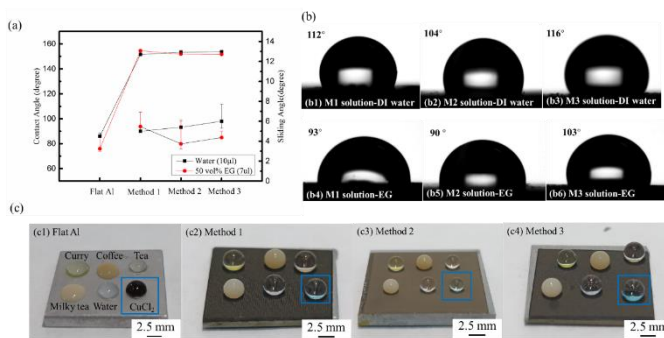


Fig. 2. (a) water and EG CAs and SAs; (b) representative CAs of the flat Al modified by three methods; (c) various liquids' wetting states on different samples.

When dropping the EG solution, the liquid stuck on the flat Al immediately and could not stream on the surface (Video S1). Conversely, the droplets would bounce off the SHS (Videos S2-S4). Furthermore, all the droplets on the flat Al spread out on the surface (Fig. 2c1). The CuCl_2 drop's color changed from blue to black because of the precipitation of Cu produced by the reaction with the Al. In Fig. 2c2-c4, all the liquids could stay a droplet state and not react to the SHSs.

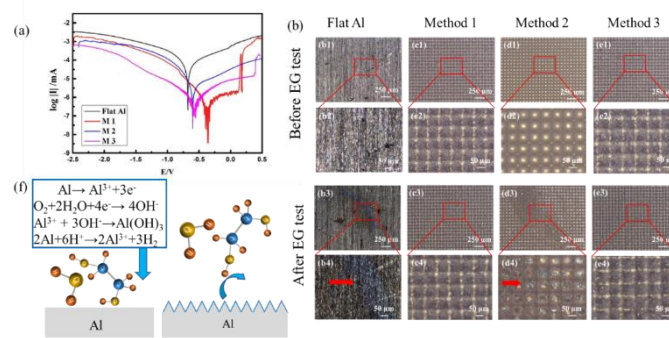


Fig. 3. Corrosion results. (a) Tafel curve of flat Al and samples by three methods modification; (b-e) surface morphologies before and after the corrosion tests; red arrows showed the surfaces' damages; (f) chemical reaction on the flat surface and SHS.

The corrosion rate (CR) and the corrosion inhibition efficiency (CIE) was calculated by the values from the Tafel curve with equation (1) and (2) (Fig. 3a). After calculation, the CR dropped by three orders of magnitude, and the CIE dropped more than 91% after chemical modification (Table S3). In Fig. 3b-e, the flat sample showed apparent damage after the corrosion test, but the SHS made by M1 and M3 showed no damage. The surface fabricated by M2 showed some damage because of the worse connection between the PDMS layer and the Al surface after laser treatment. The primary corrosion process of the EG solution is electrochemical corrosion. When the corrosion happens, it will create bubbles on the metal, called cavitation. The cavitation gradually corrodes the metal surface, making irregular holes on the surface and accelerating the metal corrosion. The side effect of EG corrosion is acid corrosion. Over time, EG will decompose or oxidize into different acids. Due to the characterization, all the results showed that the superhydrophobicity positively influences the corrosion results because of the air layer formed by the micro-nano structure and chemical layer protection (Fig. 3f).

$$R(\text{mm}/\text{year}) = \frac{3.27 \times 10^{-3} \times I_{\text{corr}} \times M}{nd} \quad (1)$$

Where M is related to the metal's atomic mass ($\text{g} \cdot \text{mol}^{-1}$), d means the metal density ($\text{g} \cdot \text{cm}^{-3}$), and n denotes the number of electrons related to the oxidizing of an atom of the element in the corrosion process.

$$\text{CIE}(\%) = \frac{I_{\text{corr}} - I'_{\text{corr}}}{I_{\text{corr}}} \times 100 \quad (2)$$

Where the I_{corr} and I_{corr}' are corrosion current density before and after.

4. Conclusion

We used three methods to get superhydrophobic Al surfaces, and all the samples showed EG CAs of more than 150° with SAs smaller than 10° . The mechanism for surface wettability change is explained by combinations between micro-nano structure formations and low surface energy. Additionally, the corrosion properties in 50 vol.% EG solution have better improvements when the samples become superhydrophobic. The CR and CIE, with noticeable drops, demonstrate their improvements. Based on the anti-corrosion performances and the sample preparations, method 1 is suggested for applying in a corrosive EG environment of a cooling system.

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Appendix A.

Supplementary data is put on the supplementary files.

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