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# Surface Modification for Anti-Adhesion Enhancement of Aluminum Alloy Using an Electrolytic Plasma

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Being a superior metal of tire mould, aluminum alloy samples were treated by an electrolytic plasma in order to improve the surface anti-adhesive properties and reduce the release force of molds. The low wettability and anti-adhesive behaviours were investigated. From photographs of SEM, the treated surface presented micro-nano binary structures. The water contact angles were measured by an optical contact angle meter, and the surface-free energy of the modified aluminum alloy was proved to be decreased. Furthermore, the effects of some process parameters, such as current densities, electrolysis plasma treating time, electrolyte temperature, and electrolyte concentration, on the low wettability of modified sample surfaces were provided. The results show that the micro-nano structures fabricated by electrolytic plasma method have an advantage in reducing the adhesion force. The hydrophilic surface was transformed into the hydrophobic surface after electrolytic plasma treatment. Consequently, it is feasible to improve the anti-adhesive property for preparing micro-nano structures and increasing contact angles on the aluminum alloy surface.

## 1. Introduction

Aluminum (Al) and its alloys are widely used materials in aerospace, automotive industries and daily life, due to excellent mechanical properties. Al and its alloys have also attracted attention as important metal substrates of tire mould. However, adhesion often presents between molds and productive parts. It is difficult to break away from molds, especially for the products adhered to deep cavities of molds. Consequently, poor adhesion resistance of Al and its alloys restricts their application into actual production.

Various surface modification techniques have been developed to improve the surface anti-adhesion. Sarkar, et al. (2008) applied chemical etching and ultrathin RF-sputter to treat aluminum surfaces, in order to obtain ultrathin Teflon films. They found that the presence of patterned morphology and ultrathin RF-sputtered coating with low surface energy, played a key role in decreasing the adhesion of aluminum surfaces. Padeste, et al. (2014) fabricated anti-sticking layers for nickel-based nano-replication tools. They concluded that evaluated anti-adhesive property of coatings relied on the low surface energy via friction force and contact angle measurements. Although above methods are sufficient effective to improve the anti-adhesion property of material surfaces, these coatings are prone to detach from the substrate surface. It brings out a degradation of the adhesion resistance.

The adhesive resistance phenomenon, known as the dung beetle, earthworm and pangolin, have attracted considerable attention because of the significant ability to keep soils from their bodies. Zhou, et al. (2005) prepared non-smooth surfaces on the steel using laser processing. The obtained non-smooth surfaces were similar to the surfaces of animal bodies, and its adhesive resistances were better than that of untreated surface. Sun, et al. (2012) found that dual roughness structure and low wettability of biomimetic units play key roles in reducing the adhesion forces. The anti-adhesive property improved with the enhancement of dual roughness structures and the increase of water contact angles on the treated surfaces. An anti-adhesive material surface usually presents a low wettability. Wettability is one of the important properties of solid surfaces, which is measured using the contact angle. Though it is feasible for above methods to fabricate anti-adhesive surfaces, laser processing is not an economical means. The contact angles obtained using the laser treatment is not larger than 120° because of the disadvantage of excessive roughness on the non-smooth surfaces. It leads the adhesive resistance to be weakened.

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A binary micro-nano structure is essential for achieving anti-adhesive surfaces on aluminum and its alloys. Several methods, such as etching, laser treatment, anodization, spin coating, electro-deposition, have been introduced to fabricate the binary micro-nano structure on the surface of aluminum or its alloys. Wu, et al. (2009) presented a new approach to obtain alumina nanowires with low adhesion, using the purely electrochemical method. The morphology and oxidation layer in treated surfaces were very robust. Siddaramanna, et al. (2014) introduced a versatile chemical deposition method to fabricate low wettability ZnO surfaces on the aluminum substrate. These above techniques are beneficial for achieving micro-nano structures on aluminum and its alloys. However, the conventional electrochemical machining requires acid corrosive liquid and takes a long time. Moreover, many fabricated adhesive resistance surfaces with binary micro-structures cannot maintain these anti-adhesive properties under harsh environmental conditions, such as high temperatures, high pressure and large wear. For many applications, the stability of the obtained anti-adhesive surfaces is very important.

In this paper, an electrolytic plasma technique is introduced to improve this stability by increasing the durability of the binary micro-structures and optimizing the chemical composition. Electrolytic plasma treatment is an unconventional kind of electrochemical machining (Gupta, Tenhundfeld, et al. (2007)). Two characteristic phenomena exist in electrolytic plasma processing. One is the electrolysis of a liquid, supplied for different electrical potentials between treating sample and a counter-electrode. The other is that plasma is generated by DC or DC pulsed electrical discharges. The main difference between electrolysis plasma and traditional electrolysis is that the former is conducted at higher voltages, whereas the latter operates at voltages in the range of 1~12 V. In this study, wetting, free energy and anti-adhesive properties of aluminum alloys are investigated by using electrolytic plasma technique. Meanwhile, the mechanical properties, such as micro-structure, roughness and microhardness also be discussed. In addition, the effects of process parameters, such as discharge voltage, electrolyte concentration, electrolyte temperature and processing time are evaluated.

## 2. Experiments

### 2.1 Experimental setup and materials

The experimental setup of anti-adhesive surface fabricated on aluminum alloys by electrolytic plasma was developed. The experiments of electrolytic plasma technique were carried out on the specially designed setup. A copper plate was used as the cathode with a size of 30 × 30 ×2 mm. A same size aluminum alloy plate was used as a workpiece anode. The distance between two inter-electrodes was 20 mm. A separate heater allowed the electrolyte temperature to be adjusted between ambient and 80 °C. A DC power supply rated at 20 KW with high voltages was introduced.

Aluminum alloys (2618) were purchased from Shanghai Hang the U. S. Metal Products Co., Ltd. A copper plate was obtained from CNMC Albetter Co., Ltd, China. Fluoroalkylsilane (tridecafluoroctyltriethoxysilane (FAS), $C_8F_{13}H_4Si(OCH_2CH_3)_3$) was supplied by Degussa Co., Germany, and the other experiment drugs, such as ethyl alcohol absolute, deionized water, ammonium citrate ($C_6H_5O_7(NH_4)_3$) and sodium sulphate ($Na_2SO_4$), purchased from Sinopharm Chemical Reagent Beijing Co, Ltd, China was of analytical grade. The electrolyte liquid was achieved by mixing $C_6H_5O_7(NH_4)_3$ and $Na_2SO_4$ into deionized water heating at temperature of 80 °C, with continuous magnetic stirring until the clear uniform electrolyte was formed.

### 2.2 Fabrication of anti-adhesive surface on aluminum alloys

The procedures for fabrication of the anti-adhesive surfaces by electrolytic plasma were shown in Figure 1.

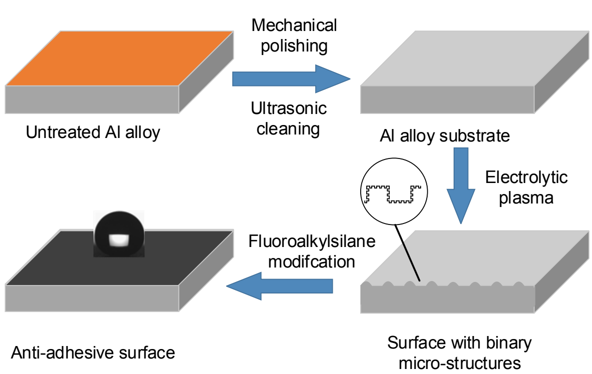


*Figure 1: Schematic of the fabrication of anti-adhesive surfaces on aluminum alloys*

Before electrolytic plasma treatment, aluminum alloy samples were polished mechanically with 800, 1200, 1500# metallographic emery paper, in order to remove contamination on the substrate surfaces. All polished samples were ultrasonically cleaned in sequence with ethanol and deionized water for 10 min, to remove any residual dust particles from their surfaces. After drying, the cleaned samples and copper cathode with the same size were positioned in parallel, and were treated by electrolytic plasma in a mixed aqueous solution of $C_6H_5O_7(NH_4)_3$ and $Na_2SO_4$ at a voltage of 400 V for 5 min. All experiments were carried out at temperature of 80 °C. The treated samples by electrolytic plasma were ultrasonically rinsed in deionized water for 10 min. Finally, they were subsequently immersed in an ethanol solution with 1.0 wt% fluoroalkylsilane (FAS) at ambient temperature for 5 h and heated at 80 °C for 30 min.

### 2.3 Characterization

The micro-nano binary structures and micro-topography of the anti-adhesive surface on aluminum alloys were presented by a scanning electron microscopy (SEM, SIRION, Holland) and an atomic force microscope (AFM, Multimode NS3a, Digital Instruments Inc.), respectively. The water contact angles were obtained from an optical contact angle meter (DSA100, Germany) at room temperature. The average value of water contact angles at three different positions of the sample surfaces can be monitored and regarded as the final contact angle. The microhardness can be measured with a peak load of 50 g for 5 s at different positions, and the average value of four microhardness values at different positions of the aluminum sample was regarded as the final microhardness. The surface roughness was measured by 3D surface profiling (CLI2000, UK). The adhesion resistances were investigated by the measured solid surface energy of the anti-adhesive surfaces.

## 3. Results and discussion

### 3.1 Surface morphology

The micro-morphology of aluminum alloy surfaces before electrolytic plasma is shown in Figure 2. Figure 2(a, b) show the SEM image of with different magnifications. Figure 2(c) shows the AFM image. In Figure 2(c), the average roughness and is about 0.31 μm. A 5 μL water droplet locates on the sample surface with a contact angle of 98.5°. Figure 3 shows the images of SEM, AFM and water droplet on sample surfaces, treated by electrolytic plasma in 8 g/L mixed aqueous solution of $C_6H_5O_7(NH_4)_3$ and $Na_2SO_4$ at 450 V voltage for 5 minutes.

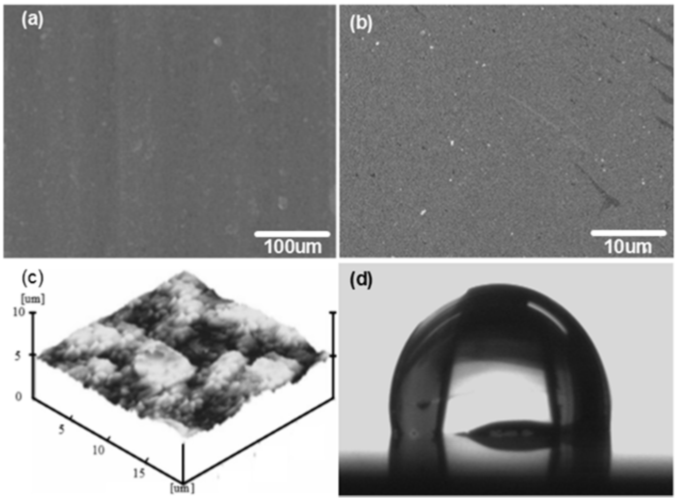


*Figure 2: Images of SEM, AFM and a water droplet on the Al alloy surfaces before treated by electrolytic plasma*

Figure 3(a) show that pit structures with diameters of 15 μm are distributed unevenly on the treated surfaces. Figure 3(b) numerous nanometer mastoids appear in the micrometer scale protrusions. Obviously, pits, caves and protrusions create micro-nano binary structures, which effectively improve the low wettability and play an important role in the following formation of anti-adhesive surfaces. Figure 3(c) shows the micro-morphologies observed by AFM, and the average roughness of treated surface by electrolytic plasma is approximately 0.409 μm. Consequently, after electrolytic plasma treatment, rough surfaces with binary micro-structures are fabricated and present low wettability after fluorination. As shown in Figure 3(d), water droplets with a contact angle of 165° exhibit a spherical shape on the modified surfaces of aluminum alloys.

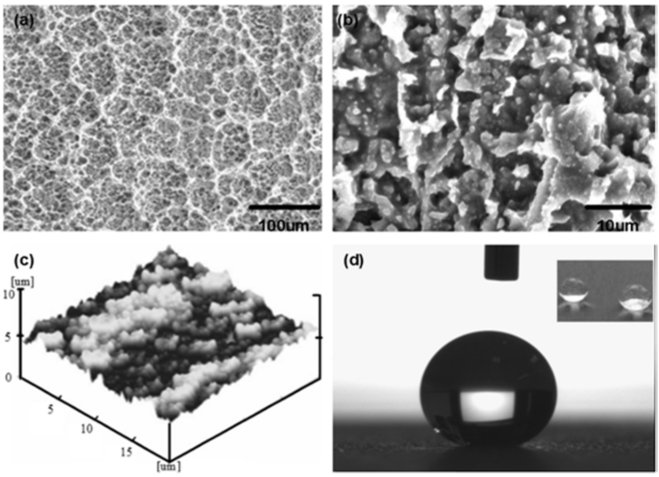


*Figure 3: Images of SEM, AFM and a water droplet on the Al alloy surfaces after treated by electrolytic plasma and FAS modification*

### 3.2 Surface wettability

The variations of contact angles and Ra obtained on aluminum alloy surfaces with electrolytic plasma depending on the process parameters, such as voltage, electrolyte concentration, processing time and fluoroalkylsilane concentration are shown in Figure 4.

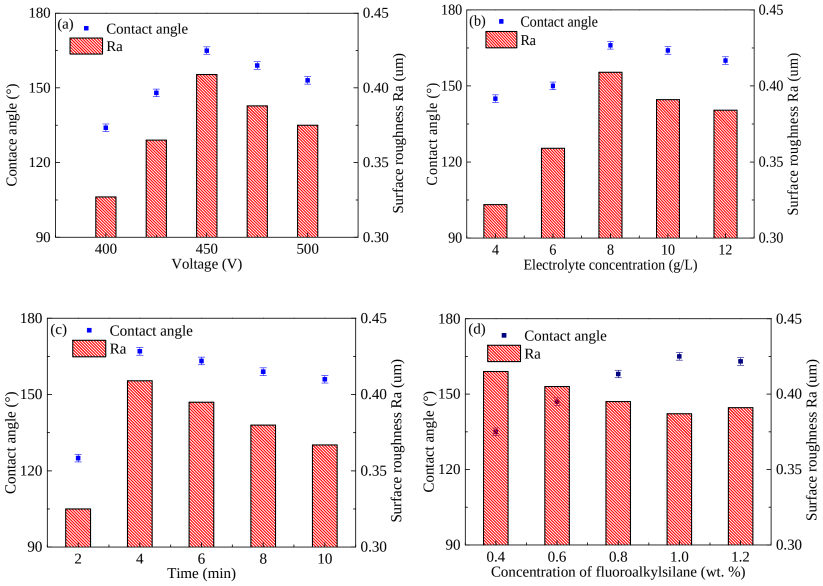


*Figure 4: Effects of different process parameters on the contact angle and Ra of the treated sample surfaces*

From Figure 4(a), it can be seen that the contact angles and Ra increase significantly with the enhancing voltage when U<450 V. This is because electrolyte active particles are not enough to form the pits or cavities (micro-nano structures) on the sample surfaces. Furthermore, the mixed aqueous solution is a nonlinear electrolyte, so a passive film is generated to prevent the sample from being corroded. Therefore, due to the large interval of round pits and non-corroded areas, there are insufficient rough structures, leading to a low contact angle. When U>450 V, the effect of micro-discharge plasma polishing is higher than that of electrolytic corrosion. The geometrical dimensions of round pits become more and more flat, which cause the average roughness Ra to be decreased. When U=450 V, There exist uniform and shallow round pits on the sample surfaces, and the fractional interfacial areas of the binary micro-nano structures are smallest. Consequently, the trapped air in the voids is biggest, and the contact angles measured on the sample surfaces increase to 166°. As shown in Figure 4(b), increasing the electrolyte concentration result in the improvement of the contact angles and Ra until the concentration reaches 8 g/L. It is because $Na_2SO_4$ is a strong electrolyte, which conductivity and electrolytic corrosion increases with the mixed electrolyte concentration. When the electrolyte concentration goes beyond 8 g/L, the interaction between the positive and negative ions increase, which results in the decline of ion's migration rate and solution conductivity. Consequently, the contact angles and Ra decrease under the effect of micro-discharge plasma polishing.

Figure 4(c) shows the variations of the contact angles and Ra with the processing time. The contact angle increases significantly until the processing time is 4 min. This reason is that a binary structure is formed by the pits and mastoids. When the processing time is more than 4 min, the contact angles and Ra become declining. This is because the prolonged treatment of electrolytic plasma is bond to restrain the active particles' generation. Meanwhile, it weakens the effect of electrolytic corrosion and destroys the formed binary micro-structures. Consequently, once the processing time is over 4 min, the contact angles and Ra are prone to decline. Figure 4(d) shows the variations of the contact angles and *R*a with the different fluoroalkylsilane concentration. The contact angles increase with the increase of fluoroalkylsilane concentration until it reaches 1.0 wt%. However, the variation of Ra has an opposite tread. This is because the $-CF_3$ and $-CF_2$ groups may be too few to generate an enough film covering the sample surface if the concentration is less than 1.0 wt. %, which would impede the free-energy decline of sample surface. Once the fluoroalkylsilane concentration goes beyond 1.0 wt. %, some white gel polymers precipitate on the sample surface.

### 3.3 Surface adhesive resistance

In order to investigate the anti-adhesive property of aluminum alloy surfaces treated by the electrolytic plasma, the adhesive energy (Landman and Luedtke (1993)) is studied by analysing the variations of surface energy. There are some methods for calculating the solid surface energy. In this study, the solid surface energies are calculated according to the concept of surface-free energy and the geometric mean method used by Ohkubo, et al. (2010). Surface free energy, which can be resolved into a London dispersive component (superscript L) and a specific (or polar, SP) component, is followed as:

$$\gamma = \gamma_S^L + \gamma_S^{SP} \quad (1)$$

where $\gamma$ is the total surface free energy, $\gamma_S^L$ is the London attraction of the van der Waals force, and $\gamma_S^{SP}$ is the other type of non-dispersive component for physical interactions. The equation used by Park, et al. (2001) is written as

$$\gamma_L(1+\cos\theta) = 2\left[\left(\gamma_S^L \gamma_L^L\right)^{1/2} + \left(\gamma_S^{SP} \gamma_L^{SP}\right)^{1/2}\right] \quad (2)$$

where $\gamma_L^L$ and $\gamma_L^{SP}$ are the dispersive component, the specific component of liquid surface free energy ($\gamma_L$), respectively. The liquid used here is re-distillation water. The characteristics of the testing liquid are listed by Wang and He (2006). The surface-free energy of the anti-adhesive surfaces on aluminum alloys can be obtained using Eq(1), Eq(2) with the measured contact angles.

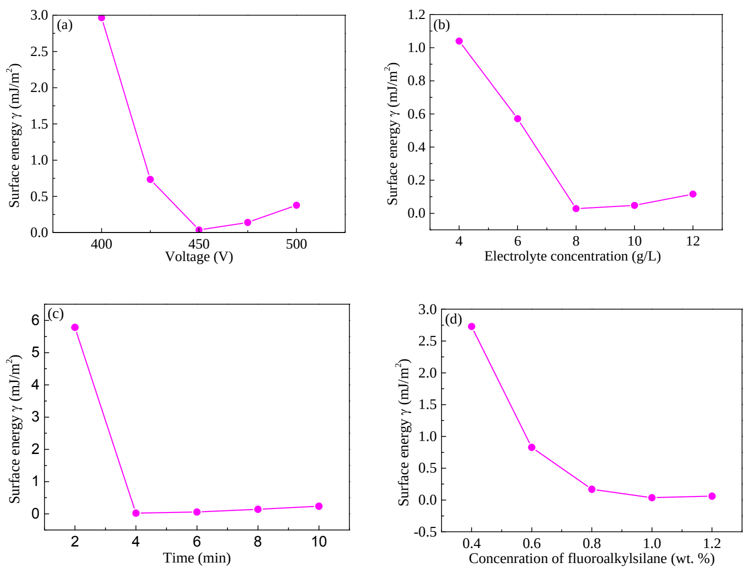


*Figure 5: Effects of different process parameters on the surface energy of the treated sample surfaces*

The changes of surface energy with different process parameters, such as voltage, electrolyte concentration, and treatment time and fluoroalkylsilane concentration are shown in Figure 5. From Figure 5, it can be found that the surface energy decrease with the increase of process parameters. When voltage, electrolyte concentration, treatment time, and fluoroalkylsilane concentration are 450 V, 8 g/L, 4 min and 0.8 wt. %, the surface energy can decline to 0.0368, 0.028, 0.0208, 0.0372 mJ/m$^2$, respectively. It can be explained by the changes of micro-structure and chemical compositions of sample surfaces. The uniform binary micro-structures can entrap air on the fabricated surface with appropriate roughness to form a steady air film, which causes the gas interfacial area fraction to increase. Therefore, the surface energy decline with the increase of contact angles. On the other hand, the increase of the chemical compositions (-$CF_3$ and -$CF_2$ groups) can also reduce the surface energy. Consequently, the uniform binary micro-nano structures fabricated by electrolytic plasma, and the chemical compositions with low surface energy groups play key roles in form the anti-adhesive surface on the aluminum alloys.

## 4. Conclusions

A stable anti-adhesive surface was successfully formed on 2618 aluminum alloy by electrolytic plasma and modification. The method used in this study presented an important inspiration on preparing the anti-adhesive surface. Immersing an aluminum alloy sample into the mixed solution of $C_6H_5O_7(NH_4)_3$ and $Na_2SO_4$ was used to fabricate micro-nano structures on sample surfaces. FAS was coated onto the treated surfaces by electrolytic plasma to reduce the surface energy of the aluminum alloy. The binary micro-structures and chemical compositions with low surface energy are the major reason for improving the adhesive resistance of aluminum alloy surfaces. Furthermore, the surface roughness, contact angle and adhesive resistance of the formed surface can be regarded easily by adjusting the voltage, processing time, electrolyte concentration and fluoroalkylsilane concentration.

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