Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2015, 7(3):449-454

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Fabrication of low wettability surfaces on aluminum substrates using electrolysis plasma treatment

Dong Xiaojuan, Meng Jianbing*, Wei Xiuting, and Yin Zhanmin

School of Mechanical Engineering, Shandong University of Technology, No.12, Zhangzhou Road, Zibo, China

---

ABSTRACT

A low wettability surface with a water contact angle of 167° and a tilting angle of 1.5° was fabricated on aluminum substrates by electrolysis plasma treatment using a mixed electrolytes of $C_6H_5O_7(NH_4)_3$ and Na_2SO_4, followed by fluorination. To optimize the fabrication conditions, several important processing parameters such as the discharge voltage, the discharge time, the concentrations of supporting electrolyte and stearic acid ethanol solution were examined systematically. Using scanning electron microscopy (SEM) to analyze surface morphology, micrometer scale pits, and protrusions were found on the surface, with numerous nanometer mastoids contained in the protrusions. These binary micro/nano-scale structures, which are similar to the micro-structures of soil-burrowing animals, play an important role in achieving low wettability properties. Otherwise, the low wettability behaviors of the resulting aluminum surfaces are analyzed by surface roughness measuring instrument, energy dispersive X-ray spectroscopy (EDS), electron probe micro-analyzer (EPMA), optical contact angle meter (CA), and digital Vickers micro-hardness (H_V) tester. The results show that the electrolysis plasma treatment is highly efficient and environmental friendly. Under the optimized conditions, the contact angle for the modified low wettability surface is up to 167°, the sliding angle (SA) is less than 2°, roughness of the sample surface is only 0.6μm. As well as, H_V is 385.

Key words: Electrolysis plasma treatment; Low wettability surfaces; Aluminum substrates

---

INTRODUCTION

Low wettability (static water droplet contact angle greater than 150°) is a very important property for functional surfaces, imparting unique characteristics such as water repellence, self-cleaning, anti-adhesion, and reduction of drag [1-3]. Many surfaces in nature exhibit low wettability. For instance, rice leaves, nepenthes' pitcher leaves [4], and other plant leaves have a self-cleaning effect. Water striders can stand effortlessly and move quickly on water [5]. Butterfly wings do not get wet in the rain [6]. The low wettability property is governed mainly by chemical modification of the surface material and the surface roughness of hierarchical micro/nano structures (cooperation of nanostructure with the microstructure). A representative example in nature of a hierarchical surface with low wettability properties is the lotus leaf [7]. The low wettability property of hierarchical structures is explainable using well-known theories, such as Wenzel and Cassie-Baxter models for a liquid drop on rough solid surfaces [8]. The water contact angle of a water droplet is dependent on the ratio of trapped air-pocket in the solid-liquid interface. For hierarchical micro/nano-structures, the area fraction of solid surface contact with a liquid is much smaller than that of single-level structure. Many methods have been used to develop fabrication technologies for hierarchical micro/nano-structures on certain metallic substrates such as Al, Cu, Zn, Ni, and Ti. Chun et al. [9] attempted to use a laser beam machining and compression molding for mass production with relatively long pulses to fabricate a transparent low wettability surface on thermoplastic polymer. Ohkubo et al. [10] fabricated low wettability surfaces on aluminum via sandblasting using grained Al_2O_3, followed by anodization in the electrolyte of phosphoric acid, and subsequent treatment with hexadecyltrimethoxysilane (HDFS). Thieme et al. [11] used siloxane rubber and epoxy resin as templates to replicate the microstructure of a lotus leaf on pure aluminum, and achieved a low wettability surface with a contact angle of 161° following chemical modification with HDFS. Qian [12] reported on the fabrication of low wettability surfaces on aluminum, copper, and zinc with dislocation etchant and fluoroalkylsilane. They found that the treated surfaces exhibit a water contact angle larger than 150°, and a tilting angle less than 10°. Shirtcliffe et al. [13] used electro-deposition and mask lithography to deposit rough copper pillars on smooth copper base surfaces in order to obtain a low wettability surface with a contact angle of 165° after coating with a fluorocarbon hydrophobic layer. These previous studies have advanced knowledge on the fabrication of low wettability surfaces on metallic substrates, but the following key issues remain to be addressed. Electro-deposition requires complex equipment, and the materials needed in electroless galvanic deposition are also costly. Anodization and chemical etching need to use a corrosive solution such as acid and alkali. Further, the one-step solution immersion method requires a longer processing time or the use of a strong alkali.

In this paper, a low wettability surface with a water contact angle of 167° and a tilting angle of 1.5° is fabricated on an aluminum substrate by electrolysis plasma treatment in a mixed electrolytes of $C_6H_5O_7(NH_4)_3$ and Na_2SO_4, followed by fluorination. Electrolysis plasma is often used to strengthen the hardness and wear resistance of aluminum and its alloys in industry. The fabrication process is based on the fact that micro/nano-scale binary structures are framed on aluminum substrates by the aid of plasma thermal polishing and electrochemical anodic dissolution. Micro-scale pit structures are framed on aluminum substrates via plasma thermal polishing treatment. Nano-scale elongated boss structures are fabricated on the micro-scale pits via electrochemical anodic dissolution. Finally, the binary structures are modified by a modifying reagent, fluoroalkylsilane, with low surface energy. This paper proposes a novel approach to fabricate low wettability surfaces on aluminum substrates. This approach could possess some advantages like simple operation steps, fast preparation speed, low roughness and high surface hardness.

EXPERIMENTAL SECTION

1.Materials

The objectives of this research were to develop an economical process for manufacturing low wettability surfaces, and to understand the effects of processing parameters on low wettability of aluminum substrates. An aluminum plate with purity C 99% (Cu 0.005 wt. %, Fe 0.003 wt.%, Si 0.0025 wt.%) was obtained from Aluminum Corporation of China. A copper plate was obtained from CNMC Albetter Albronze Co., Ltd, China. Fluoroalkylsilane (tridecafluoroctyltriethoxysilane (FAS), $C_8F_{13}H_4Si(OCH_2CH_3)_3$) was obtained from Degussa Co., Germany, and the other experiment drugs used were of analytical grade (Tianjin Kermel Chemical Reagent Co., China).

2.Fabrication of the low wettability surfaces

A mixed aqueous solution of 4-12 g/L was obtained by adding a certain amount of $C_6H_5O_7(NH_4)_3$ and Na_2SO_4 into 1L of deionized water. Through addition of 1 g FAS into 99 g anhydrous ethanol at room temperature in a beaker, followed by stirring with a magnetic stirrer at a speed of 100 r/min for 2 h, 0.4-1.2 wt.% fluoroalkylsilane–ethanol solution was prepared. An aluminum plate (20×10×2 mm) was polished mechanically using $300^{\#}$ and $1000^{\#}$ metallographic abrasive papers, and cleaned ultrasonically in sequence with alcohol and deionized water. After drying, the anodic aluminum plate and cathodic copper plate with the same size as the anode were parallel positioned with a distance of 10 cm. Then the aluminum plate was machined by electrolysis plasma in the 4-12 g/L $C_6H_5O_7(NH_4)_3$ and Na_2SO_4 aqueous solution at a voltage of 300-500 V for 2–10 min at room temperature. After machining, the specimens were ultrasonically rinsed with deionized water for 5 min and dried. Modification of the aluminum specimens with low surface energy material was performed by dip-coating them in 0.4-1.2 wt.% fluoroalkylsilane–ethanol solution for 3 h at room temperature, followed by heat-treated at 90°C for 20 min.

3.Characterization of the low wettability surfaces

The morphological and elemental analyses of the samples were performed using a scanning electron microscopy (SEM, SIRION, and Holland), an energy dispersive X-ray spectroscopy (EDS, INCA Energy, UK) and an electron probe micro-analyzer (EPMA 1720, Shimadzu, Japan). Water contact angles and tilting angles were measured by an optical contact angle meter (DSA100, Germany) at ambient temperature. Water droplets of 5μL were dropped carefully onto the surfaces and the average value of three measurements at different positions of the samples was adopted as the final contact angle. The tilting angle is defined as the angle at which the water drop begins to roll off the gradually inclined surface. Micro-hardness of the sample surfaces was measured using digital Vickers micro-hardness tester (570HAD, China) and the average value of five measurements with a peak load of 50 g for 5 s at different positions was taken as the final micro-hardness. The surface roughness was measured by 3D surface profiling (CLI2000, UK). The surface roughness was measured by 3D surface profiling (Talysurf CLI2000, UK).

RESULTS AND DISCUSSION

1.Microstructures of the treated aluminum surface

Figure 1 shows the SEM images of the aluminum surfaces treated by electrolysis plasma in 8 g/L $C_6H_5O_7(NH_4)_3$ and Na_2SO_4 aqueous solution at 480V DC voltage for 4 min, as well as images of the water droplets on the as-prepared aluminum surface treated with fluoroalkylsilane.

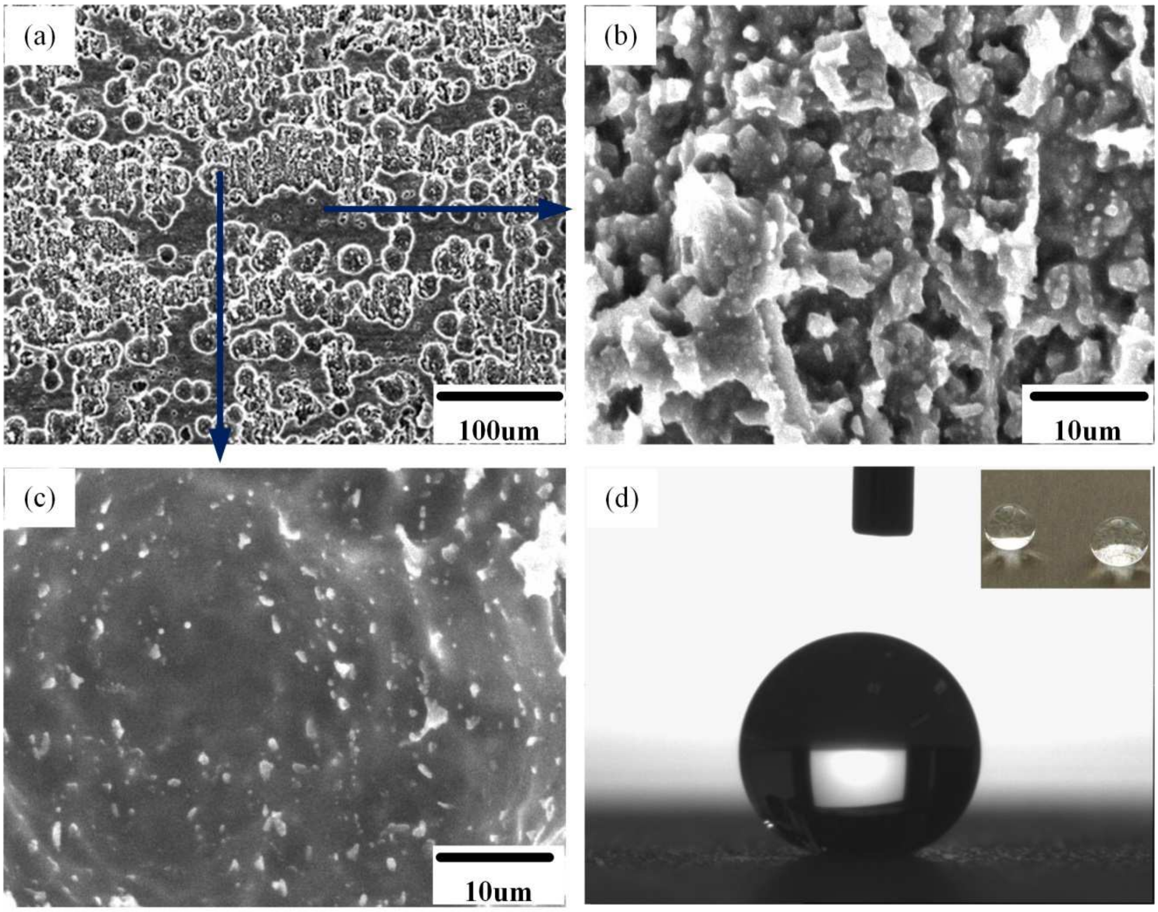

Fig.1 SEM images of the aluminum surfaces after processing and optical image of the droplets on the as-prepared surfaces with a ×200 magnification; b ×2,000 magnification image of the fractal structures; c ×5,000 magnification image of the round pits; d water droplet with a volume of 5μL

Fig. 1a shows the image with 200× magnification. It can be seen that pit structures with diameters of 10-20μm are distributed unevenly on the aluminum surface. Fig. 1b shows the image of the fractal rough structures with 2,000× magnification. A micro-scale structure which consists of connected anomalistic micrometer scale caves and protrusions is fabricated. As shown in Fig. 1b, numerous nanometer mastoids are contained in the micrometer scale protrusions. Fig. 1c shows the round pits in Fig. 1a with 5,000× magnification, indicating that nanometer grains exist on wall of the round pits. As shown in Fig. 1d, a 5 water droplet of 5 μL exhibits a typical spherical shape with a contact angle of 158° and a tilting angle of 2° on the anti-adhesion surface. This low wettability behavior can be explained theoretically in terms of the Cassie-Baxter model, which is described as follows:

$$\cos\theta_c = f_1 \cos\theta - f_2 \quad (1)$$

Whereθ_c (167°) and θ (108°) represents the contact angles on the rough and smooth aluminum surfaces, respectively, which are both modified by fluoroalkylsilane. f_1 and f_2 are the fractional interfacial areas of the binary micro/nano-scale structures and of the trapped air in the voids among the binary structures, respectively (f_1+f_2=1). From this equation, we can deduce that an increase in the fraction of air (f_2) can increase the contact angle of the binary structures surface (θ_c). According to the equation, f_1 and f_2 are estimated to be 0.037 and 0.963, respectively. Therefore, when a water droplet is placed on the anti-adhesion surface on aluminum, only about 3.7% serves as the contact area of the liquid droplet and the solid surface, and the remaining 96.3% serves as the contact area of the liquid droplet and air.

2.Low wettability of the treated aluminum surface

The chemical compositions of the anti-adhesion surface were analyzed using EDS and EPMA, as shown in Fig. 2a and Fig. 2b. The anti-adhesion surface is mainly composed of element Al, C, Si, O and F, which indicate that the hydrophobic fluoroalkylsilane coating has been self-assembled on the aluminum surface. As a conclusion, the binary micro/nano-scale rough structures allow large amount of air entrapment making it a heterogeneous surface composite of air and the surface where the air and the self-assembled film of fluoroalkylsilane contributes to low surface energy weakening its interaction with liquid and therefore enhancing the low wettability.

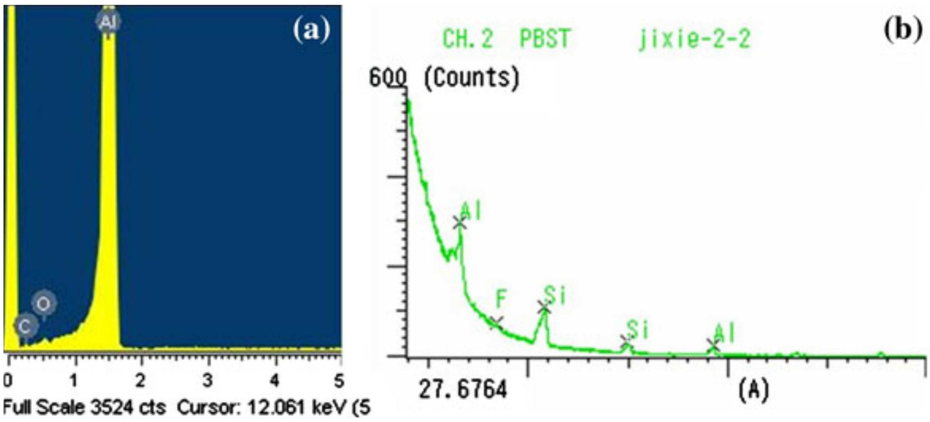

Fig.2 EDS and EPMA spectra of the anti-adhesion surface on aluminum substrates

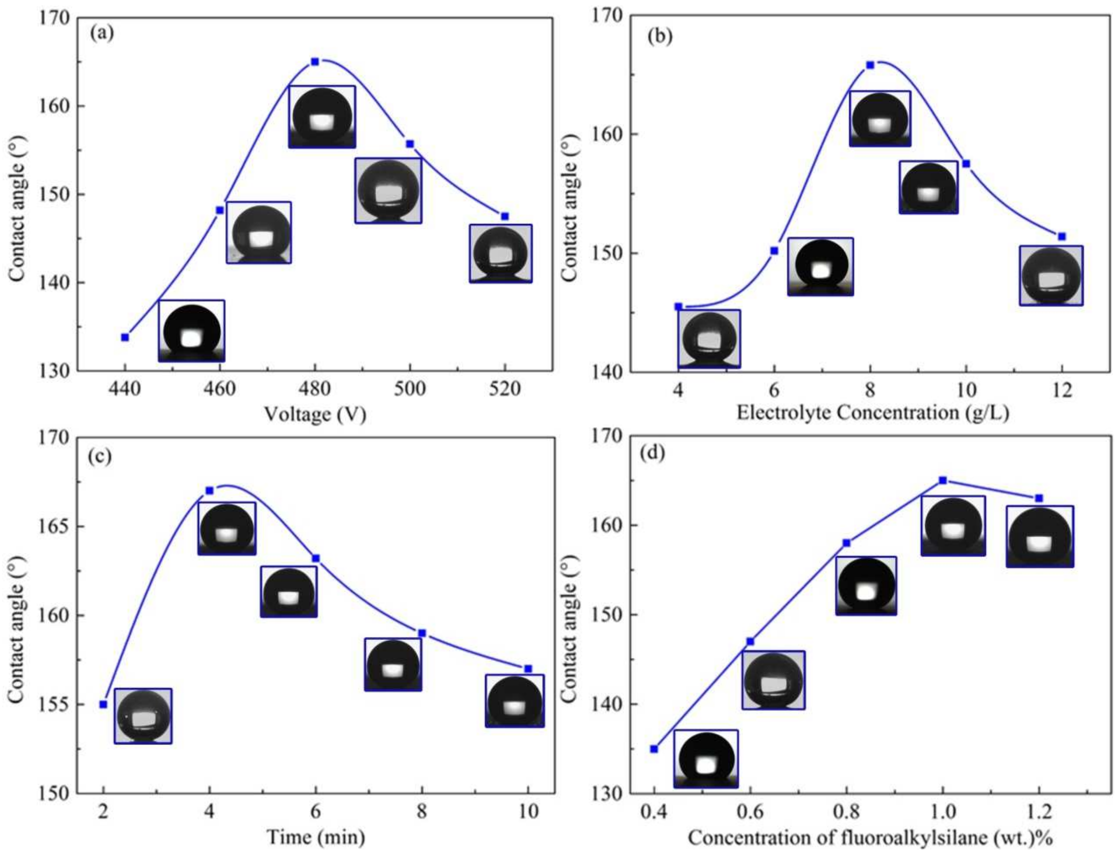

Fig.3 Relationship between processing parameters and contact angle on the wetting properties

3.Effects of processing parameters on low wettability

Figure 3 shows the effect of the variation of processing parameters on the wettability of the anti-adhesion surface obtained by the electrolysis plasma treatment. As shown in Fig. 3a, the contact angle increases significantly with an increase in the processing voltage from 440-480V. This is because the thermal polishing corrosion and electrolyte active particles, resulting from the micro-discharges, are not enough to form the pits or cavities on the aluminum substrate. Furthermore, the $C_6H_5O_7(NH_4)_3$ and Na_2SO_4 aqueous solution is a nonlinear and passive electrolyte, so a passive film is generated on aluminum surface to prevent the sample from being corroded when the processing voltage is less than 480V and a low voltage efficiency. 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 the processing voltage is 480V, there exist uniform and shallow round pits on the sample surfaces. This is due to the increase in thermal corrosion amount and active particles with an increase in voltage efficiency. However, when the processing voltage goes beyond 480V, the contact angle decreases significantly. This is because the thermal corrosion and active particles are so much that uniform pits are polished and rough structures become more and more smooth. Consequently, the contact angle of the sample surface decreases with the decrease of f_2.

Fig. 3b shows the variation in water contact angle with $C_6H_5O_7(NH_4)_3$ and Na_2SO_4 concentration. Wettability is affected significantly by the mixed electrolyte concentration. It is because Na_2SO_4 is a strong electrolyte, which conductivity and electrochemical anodic dissolution increases with the mixed electrolyte concentration in the range of 4 to 8 g/L. When the electrolyte concentration goes beyond 8 g/L, the interaction between the positive and negative ions increase, which results in the decline of ions migration rate and solution conductivity. Consequently, the water contact angle reaches165.8° and a titling angle is less than 2° as shown in Fig. 3b, when electrolyte concentration is 8 g/L.

Fig. 3c shows the variation in water contact angle with the processing time. The contact angle increases significantly with an increase in processing time from 2 to 4 min. the contact angle of the treated surface after 4 min of processing and fluoroalkylsilane modification reaches 167°, because a certain roughness is obtained from the micro-scale pits and nano-scale mastoids after electrolysis plasma machining. When the processing time is more than 4 min, the contact angle becomes to decline. This is because the time of micro-discharge in electrolysis plasma treatment affects the number of thermal corrosion and active particles, which play a key role in the diameter of the pits and the distribution of the mastoids. Consequently, excessive micro-discharge of electrolysis plasma severely affects the micro/nano-scale binary structures and weakens the low wettability of treated aluminum surface.

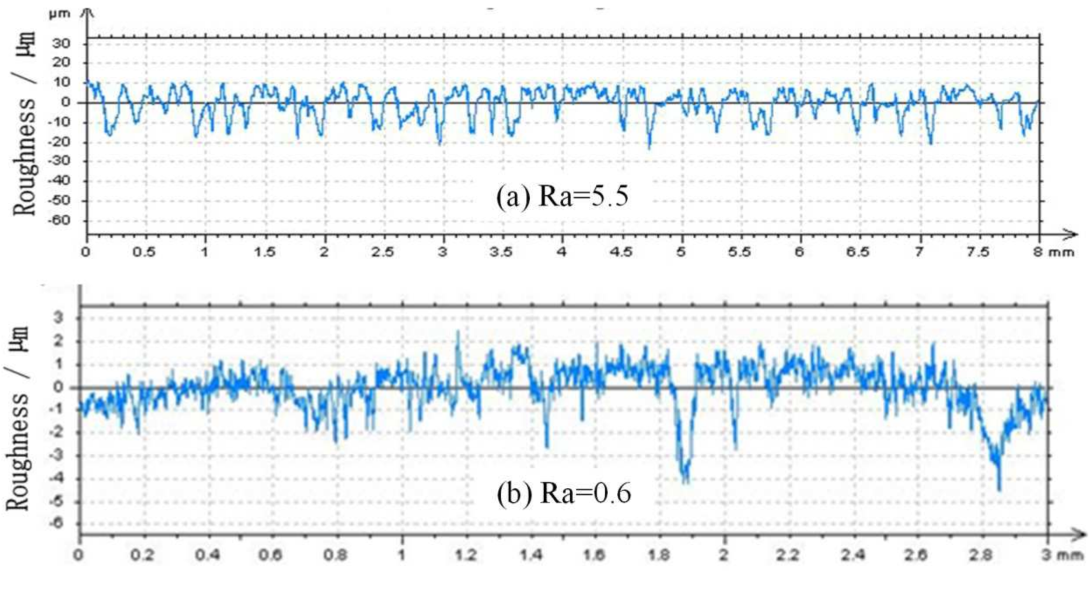

Fig.4 The roughness of low wettability surfaces on substrates using the etching method (a) and electrolysis plasma machining method (b)

Fig. 3d shows the variation in water contact angle with the concentration of fluoroalkylsilane in the range of 0.4 to 1.2 wt.%. The water contact angle rapidly increases with the increase of fluoroalkylsilane concentration in the range of 0.4 to 1.0 wt.%. This is because the $-CF_3$ and $-CF_2$ groups may be too few to form a 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. However, when the fluoroalkylsilane concentration goes beyond 1.0 wt.%, some white gel polymer appears to precipitate on sample surface. Therefore, the gel polymer would significantly weaken low wettability and cause the decrease of the water contact angle on the treated aluminum surface.

4.Roughness and mechanical strength of the low wettability surfaces

Figure 4(a) is the roughness of the low wettability surfaces obtained by Sarkar's method [14]. The roughness Ra of the aluminum after hydrochloric acid etching is about 5.5 µm, and the structures of the surface are easily damaged by slight scratching. Figure 4(b) is the roughness of the low wettability surfaces obtained using the electrolysis plasma machining.

It can be seen that the roughness Ra is about 0.409 µm and less than that of Sarkar's. This roughness prepared using electrolysis plasma treatment is also far less. As the main components of the aluminum substrate surfaces are alumina, so the hardness is improved significantly. Surface hardness measurements show that the micro-hardness of the aluminum substrate increases monotonically from 30 H_V at 0 min to 220 H_V at 2 min, and finally to 385 H_V after 4 min.

CONCLUSION

Low wettability surfaces with a water contact angle of 167° and a tilting angle of 1.5° were fabricated on aluminum substrates by electrolysis plasma machining using a mixed electrolytes of $C_6H_5O_7(NH_4)_3$ and Na_2SO_4, followed by fluorination. Compared with traditional methods, the method proposed in the current paper does not require a strong acid and a strong base. It is also advantageous in that it does not require complex and expensive device system, and is highly efficient and environment friendly. The low wettability behavior is explained theoretically in terms of the Cassie-Baxter model. Only about 3.7% serves as the contact area of the water droplet and the solid surface.

Low wettability on an aluminum substrate is generated by micro/nano-structures, such as pits, cavies and protrusions, which are assumed to be caused by the plasma thermal corrosion and the preferential dissolution of grain boundaries by an applied electric field. Processing parameters such as processing voltage, electrolyte concentration, processing time and concentration of fluoroalkylsilane were investigated to determine their effect on low wettability of aluminum surfaces. The optimum processing conditions were a processing voltage of 480 V, a $C_6H_5O_7$ $(NH_4)_3$ and Na_2SO_4 electrolyte of 8 g/L, a processing time of 4 min, and fluoroalkylsilane concentration of 1.0 wt. %.

Acknowledgements

Part of this work is supported by the National Natural Science Foundation of China (Grant No. 51205237 and 51375284), the natural science foundation of Shandong Province (ZR2014EEQ019), the young teacher development support plan of Shandong University of Technology, and young college teachers international visiting scholars plan of Shandong Province.

REFERENCES

[1] V.A. Ganesh, H.K. Raut, A.S. Bair, S. Ramakrishna, *Journal of Materials Chemistry*, 21 (**2011**) 16304-16322.
[2] X. Yao, Y. Song, L. Jiang, *Advanced Materials*, 23 (**2011**) 719-734.
[3] D.H. Chu, A. Nemoto, H. Ito, *Microsystem Technology*, 20 (**2014**) 193-200.
[4] B. Ulrike, G. Ulmar, F. Walter, *Journal of Experimental Biology* 62 (**2011**) 3683-3692.
[5] X.F. Gao, L. Jiang, *Nature*, 432 (**2004**) 36-36.
[6] H. Wang, L.M. Tang, X.M. Wu, W.T. Dai, Y.P. Qiu, *Applied Surface Science*, 253 (**2007**) 8818-8824.
[7] B. Cortese, S. D'Amone, M. Manca, I. Viola, R. Cingolani, G. Gigli, *Langmuir*, 24 (**2008**) 2712-2718.
[8] A. Cassie, S. Baxter, *Transactions of the Faraday Society*, 40 (**1944**) 546.
[9] D.M. Chun, G. Davaasuren, C.V. Ngo, C.S. Kim, G.Y. Lee, S.H. Ahn, *CIRP Annals – Manufacturing Technology*, 63 (**2014**) 525-528.
[10] Y. Ohkubo, I. Tsuji, S. Onishi, K. Ogawa, *Journal of Materials Science*, 45 (**2010**) 4963-4969.
[11] M. Thieme, R. Frenzel, S. Schmidt, F. Simon, A. Hennig, H. Worch, K. Lunkwitz, *Advanced Engineering Materials*, 3(**2001**) 691-695.
[12] T. Liu, Y.S. Yin, S.G. Chen, X.T. Chang, S. Cheng, *Elecrochimica Acta* 52, (**2007**) 3709-3713.
[13] B.T. Qian, Z.Q. Shen, *Langmuir*, 21 (**2005**) 900799009.
[14] D.K. Sarkar, M. Farzaneh, R.W. Paynter, *Materials Letters*, 62 (**2008**) 1226-1229.