Colloids and Surfaces A: Physicochem. Eng. Aspects 499 (2016) 150–155

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Combined wet chemical etching and anodic oxidation for obtaining the superhydrophobic meshes with anti-icing performance

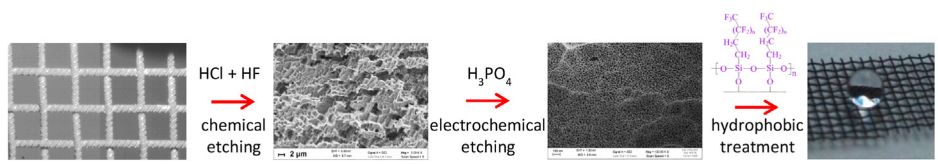
Agatha Ganne, Valeria O. Lebed, Anton I. Gavrilov*

A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky Prospect 31 Bldg. 4, 119071 Moscow, Russia

HIGHLIGHTS

- Combined chemical etching and anodic oxidation result in multimodal roughness.
- Superhydrophobic meshes show hours of freezing delay for deionized and salt water droplets.
- Fabricated coatings show high stability against prolonged contact with gasoline and water.
- The superhydrophobic meshes demonstrate high anti-icing performance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 March 2016
Received in revised form 6 April 2016
Accepted 6 April 2016
Available online 7 April 2016

Keywords:
Surfaces
Coatings
Etching
Freezing delay
Surface properties

ABSTRACT

The superhydrophobic state of surface of AMG2 aluminum alloy meshes was obtained by wet chemical etching in mixture of HCl and HF, anodic oxidation in phosphoric acid solution, and chemisorption of fluorooxysilane. Testing of fabricated coatings against long term contact with high-octane gasoline and water indicates very high chemical resistance of superhydrophobic coatings. The anti-icing potential of fabricated superhydrophobic meshes with respect to deionized and salt water was estimated by analysing the work of adhesion of supercooled droplets, the adhesion of iced droplets to the superhydrophobic mesh, and the freezing statistics. The detected freezing delay for both deionized and salt water amounts several hours allowing the removal of the droplets before freezing due to their rolloff under wind or vibration loads.

1. Introduction

Aluminum and its alloys have a very broad range of engineering applications, including aviation, automobiles, construction, heavy and light industries, home appliances and electronic devices etc. However, the outdoor exploitation of machinery and equipment in cold weather seasons can meet considerable impediments because of ice and snow accretion on working surfaces. Therefore it is still a big challenge for both the material scientists and industrial engineers to create the surfaces which may effectively resist icing in cold environments, and the problem of preventing ice/snow accretion or mitigating its effect on operation of various equipment is a central topic of many studies [1–7]. Among other approaches to solve the problem, the use of superhydrophobic surfaces [1–4,7] seems to be very promising as a passive protection acting without necessity of external triggering (in contrast to active methods which require regular application of anti-icing liquids or supply of thermal/mechanical energy to melt/remove accreted ice). In particular, the superhydrophobic meshes, which have already found a great deal of applications for oil-water separation, can also be considered as potentially effective elements for engine air intake devices for aviation, shipbuilding or motor-car construction. Plenty of

* Corresponding author.
E-mail addresses: anton.i.gavrilov@yandex.ru, 9554625@mail.ru (A.I. Gavrilov).

http://dx.doi.org/10.1016/j.colsurfa.2016.04.019
0927-7757/

various methods of surface treatment were developed in the literature to meet the dual prerequisite for achieving the superhydrophobic state, namely, to create the multimodal surface roughness and to essentially decrease the material surface energy [8–24]. Among others, the wet chemical etching and anodic oxidation attract particular attention as simple, adaptable for industrial applications and non-expensive methods [9–12]. The aim of this study is to obtain the superhydrophobic state of aluminum meshes and plates, characterized by robust anti-icing properties in contact with humid atmosphere, deionized and salt water.

2. Experimental

2.1. Materials and sample preparation

Aluminum alloy meshes (#30) and sheets (1 mm thickness) were obtained from The Kharkov Frunze Plant PSC (Ukraine). The used AMG2 alloy composition (in mass%): Al-96.2; Mn-0.35; Fe-0.5; Si-0.4; Cu-0.15;Mg-2.0; Cr-0.0.5; Zn-0.15; Ti-0.05. The acids of analytical grade were purchased from Mosreactiv, Russia. For the hydrophobization of surfaces we have used methoxy-{3-[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)-oxy]-propyl}-silane, synthesized by prof. A.M. Muzafarov (the details of synthesis are presented in Ref. [25]), as a hydrophobic agent, and 99% decane (Acros Organics) as a solvent.

Aluminum alloy meshes were cut in pieces of 80 mm × 80 mm, and sheets were cut in plates of two sizez: 10 mm × 10 mm, and 80 mm × 80 mm. Samples were washed in ethanol and deionized water during 1 min using ultrasonic bath, and air dryed. Two different protocols were used to impart the necessary surface texture. According to the first one (hereinafter denoted as the **Protocol 1**), the samples were immersed in the etching solution containing HF(40%), HCl, and H_2O in the proportion −1:10:6 for 1–3, or 5 min. The lowering of surface energy of textured samples, both grids and sheets, was performed by the chemisorption of methoxy-{3-[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8- pentadecafluorooctyl)-oxy]-propyl}-silane from the solution in decane, as it was described in Ref. [26]. It was shown [26] that this hydrophobic agent demonstrates high stability against desorption and hydrolysis at long term contact with aqueous phases. According to the second protocol (**Protocol 2**) the samples were textured by the two-step procedure. First, the samples were immersed in the etching solution containing HF (40%), HCl, and H_2O in the proportion −1:10:6 for 2 min. It will be shown below, that this time of wet etching provides the best outcome in the first protocol. Then the samples were washed in deionized water three times during 1 min each, using an ultrasonic bath. On the next step the anodic oxidation in the galvanostatic regime in a 20 w.% phosphoric acid solution at room temperature was performed during 5 min. After anodic treatment the samples were washed with distilled water, and dryed in an oven at 130 °C during 1 h. The lowering of surface energy of textured meshes was performed by the chemisorption [26] of methoxy-{3-[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)-oxy]-propyl}-silane from the solution in decane. For the reference, two samples (one plate and one mesh) without any texturing treatment were hydrophobized by the chemisorption of the same hydrophobic agent followed by drying in an oven at 130 °C for 1 h.

2.2. Characterization

Water contact angles of samples after treatment were measured using the setup [27], based on the method of Laplace fitting procedure for digitized droplet profile [28]. To study the robustness

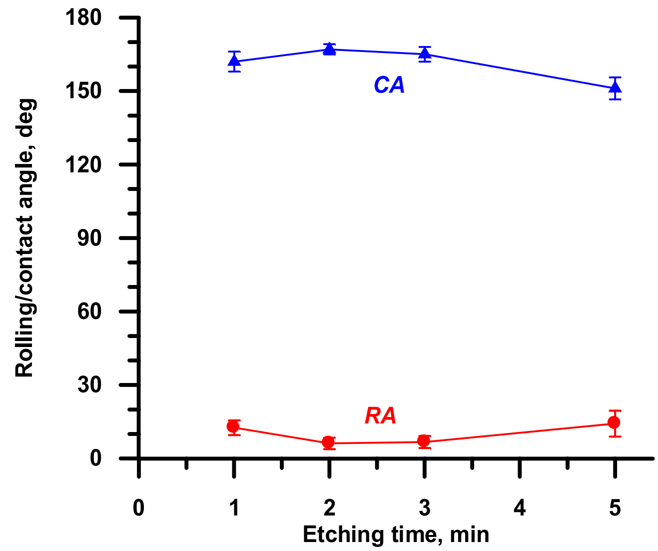


Fig. 1. Contact angles (CA) and rolling angles (RA) for superhydrophobic aluminum plate surfaces, obtained according to the **Protocol** 1, with different time of chemical etching.

of superhydrophobic coatings to long term contact with aqueous phase and humid atmosphere we used the double wall cell developed in our lab earlier [29]. Very attractive advantage of this cell is its ability to maintain 100% humidity and thus to prevent the droplet evaporation. Using this cell we have monitored the evolution of the contact angle for water/brine solution droplet deposited onto the mesh. The wettability of the individual wire, used to fabricate the mesh, was measured by "a drop on a filament" method. This method was developed in Ref. [30] and is based on the digital image processing of the profile of axisymmetric droplet of liquid, suspended on vertical filament. The freezing delay for the ensemble of sessile droplets, deposited onto the superhydrophobic meshes and plates was studied according to the methodics developed and described in detail in Ref. [29]. Since the droplet freezing is a stochastic process, the analysis of statistics required large number of droplets [31], and typically we have analyzed the data using 150–250 droplets with the volume of 15 µL each. Experiments at negative temperatures were performed in a Binder MK53 Environmental Chamber. The surface morphology of the samples was studied by a Supra 40 VP field emission scanning electron microscope (Carl Zeiss).

3. Results and discussion

The advancing contact angles measured for bare (non- treated) alloy wire and bare plate are given in Table 1 and, being less than 90°, indicate the hydrophilic nature of bare aluminum alloy surface.

In Fig. 1 the contact and rolling angles are presented for the superhydrophobic plates subjected to chemical etching according to the **Protocol 1**, for different etching times. The decrease in contact angles obtained for the samples etched more than 2 min is seemingly associated with rapid heating of etching solution (by released heat of exothermic chemical reaction). This overheating may affect the chemical dissolution and cause a decrease in effective roughness of produced surface morphology.

The data presented in Fig. 1 indicate that surface texturing by chemical etching in the acidic solution allows obtaining the superhydrophobic state for all etching times considered. However, the etching time of 2 min was chosen, as leading to the highest contact angle and the smallest rolling angle. The values of advancing contact angles and rolling angles characteristic of the superhydrophobic aluminum alloy plates and meshes obtained for the