

Superhydrophobic Aluminum Alloy Surfaces by a Novel One-Step Process

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ABSTRACT A simple one-step process has been developed to render aluminum alloy surfaces superhydrophobic by immersing the aluminum alloy substrates in a solution containing NaOH and fluoroalkyl-silane (FAS-17) molecules. Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and water contact angle measurements have been performed to characterize the morphological features, chemical composition and superhydrophobicity of the surfaces. The resulting surfaces provided a water contact angle as high as $\sim 162^\circ$ and a contact angle hysteresis as low as $\sim 4^\circ$. The study indicates that it is possible to fabricate superhydrophobic aluminum surfaces easily and effectively without involving the traditional two-step processes.

KEYWORDS: one-step process • superhydrophobicity • aluminum alloy • water contact angle • contact angle hysteresis • scanning electron microscopy • X-ray photoelectron spectroscopy

INTRODUCTION

Superhydrophobicity, found on many natural surfaces, the most classic example being the lotus leaf, has inspired researchers around the world for its importance in fundamental research as well as its potential in industrial use. The key element in the inherent water repellency on the lotus leaf surface is the presence of a low surface energy hydrophobic surface coating (epicuticular wax crystalloids) on a microscopically rough structure (1). The tremendous importance of superhydrophobic surfaces in areas such as antibiofouling paints for boats, biomedical applications, microfluidics, corrosion resistance, stain resistant textiles, inhibition of ice or snow adhesion, oxidation, drag reduction (2–7), etc., has inspired mankind to replicate nature.

The traditional way of making superhydrophobic surfaces involves two steps (8–11). In this method, a certain rough micronanopattern is first created and the patterned rough surface is then passivated using a low surface energy coating to lower the surface energy, reducing the affinity of water drops to the surface. We have previously prepared several superhydrophobic surfaces via a two-step procedure, using techniques such as chemical bath deposition (CBD), substrate chemical etching, galvanic exchange reactions, etc., to create the surface roughness and then passivating those using organic molecules such as stearic acid, fluoroalkyl-silane molecules or by coating with rf-sputtered Teflon (8–11). All these studies emphasized the importance of the coexistence of both surface roughness and the low surface

energy coating in order for the surfaces to exhibit superhydrophobicity. Therefore, if both surface roughness and low surface energy could be obtained in just one single step, the complexity of involving two steps in creating superhydrophobic surfaces can be eliminated. Very recently, we have demonstrated that superhydrophobic silver films on copper (Cu) substrates can be created in a one-step process via galvanic reactions by immersing the Cu substrates in a silver nitrate solution containing fluoroalkyl-silane (FAS-17) (12). The incorporation of low surface energy compounds during the creation of surface roughness, therefore, can lead to superhydrophobic surfaces in just one step. The aluminum industry can greatly benefit from such easy treatments where corrosion is a concern.

In the present study, we report the creation of superhydrophobic properties on aluminum alloy surfaces treated with fluoroalkyl-silane (FAS-17) in sodium hydroxide (NaOH) solution. The SEM studies reveal the presence of a rough micropattern on the treated surfaces and the XPS studies confirm the presence of FAS-17 molecules.

EXPERIMENTAL DETAILS

Aluminum alloy coupons (AA6061 alloy) were ultrasonically degreased in 1 % Liquinox solution for 10 min followed by ultrasonication with deionized water, twice for 10 min each time. The clean Al coupons were simply immersed in beakers containing a mixture of 0.1 M sodium hydroxide (NaOH) and 400 mM fluoroalkyl-silane ($\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OC}_2\text{H}_5)_3$ (FAS-17) at varying FAS-17 to NaOH ratios and placed in an ultrasonic bath for 30 min followed by a rinse in deionized water and subsequent drying in air for several hours prior to further characterization. The morphological and elemental analyses were performed using a scanning electron microscope (SEM/EDX, JEOL JSM 6480 LV). The rms roughness of the resulting surfaces was measured using an AD phase shift

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Received for review July 5, 2010 and accepted August 26, 2010

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DOI: 10.1021/am100563u

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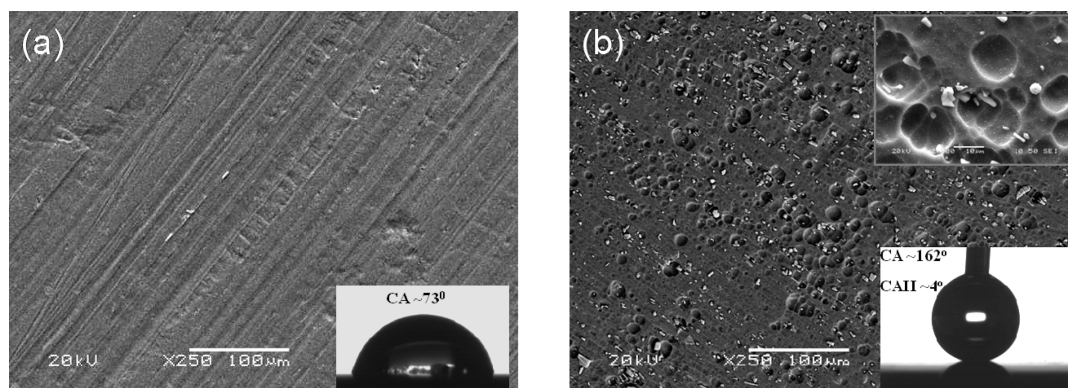


FIGURE 1. SEM images of aluminum surfaces (a) as-received (inset shows the water drop image on a) and (b) treated with NaOH and FAS-17 (inset shows a magnified SEM image of b as well as a water drop image on b).

optical profilometer. The surface chemical compositional analyses were performed by X-ray photoelectron spectroscopy (XPS, VG ESCALAB 220iXL). The XPS spectra were collected by using an Al K_{α} (1486.6 eV) X-ray source. These samples were tested for superhydrophobicity using a contact angle goniometer (Krüss GmbH, Germany). The contact angle data were acquired by fitting the symmetric water drops using the Laplace–Young equation and the advancing and receding contact angles were measured by fitting the asymmetric water drops using the tangent-2 method. The difference between the advancing and receding contact angles provide the contact angle hysteresis.

RESULTS AND DISCUSSION

A chemical reaction of NaOH with aluminum in the presence of FAS-17 molecules results in an etching process leading to a rough microporous structure on the surface as shown in the SEM image of Figure 1b. The figure represents the aluminum surface treated with NaOH in the presence of FAS-17 molecules at a F/OH ratio of 0.4, revealing craterlike microfeatures evolved following treatment, as compared to the as-received clean aluminum surface shown in Figure 1a. Further SEM analyses also revealed that the morphological features remained similar on all surfaces treated with or without FAS-17 molecules. The formation of a rough microcratered surface, in combination with a modified surface chemistry arising from the adhesion of FAS-17 molecules, contributes to the creation of superhydrophobic properties.

XPS investigations of the aluminum surfaces treated with NaOH and FAS at different F/OH ratios revealed the presence of C, F, O, and Si with no trace of Na in the survey spectra (see the Supporting Information). Figure 2 shows the high-resolution C 1s core level spectrum acquired from the aluminum surface treated with a F/OH ratio of 0.4, resolved into seven components, namely, $-\text{CF}_3$ (293.82 eV), $-\text{CF}_2$ (291.22 eV), $-\text{CH}_2-\text{CF}_2$ (288.82 eV), $-\text{C}-\text{O}$ (286.14 eV), $-\text{C}-\text{C}$ (285 eV), $-\text{C}-\text{Si}$ (281.78 eV) and $-\text{C}-\text{metals}$ (280.21 eV). The F 1s peak was observed at a binding energy of 688.5 eV. These results are consistent with the results reported by Sarkar and Paynter (12). The CF_3 and CF_2 concentrations from the spectra (Figure 2), which are 6.16 and 47.71 %, respectively, are slightly higher than the theoretical values

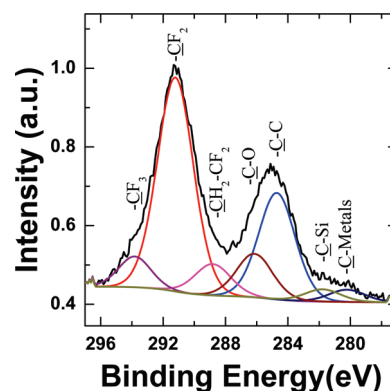


FIGURE 2. High-resolution C 1s core level spectrum of FAS-17/NaOH-treated Al surface.

obtained from the molecular structure of FAS-17, which are 6 and 41 %, respectively, indicating that the low-surface-energy CF_3 and CF_2 components comprise the outermost surface contributing to superhydrophobic properties.

On the other hand, an analysis of the binding energies of the O 1s, Al 2p, and Si 2p peaks indicate a possible bonding mechanism of FAS molecules with the Al substrate (see the Supporting Information). In the hydrolysis process, the removal of C_2H_5 from the FAS-17 molecules may give rise to the formation of $\text{Si}-\text{O}-\text{Al}$ bonding at the substrate. The binding energy of the O 1s core level peak found at 531.7 eV is comparable to the binding energy of the O 1s peak in the metal silicate (15). Sarkar and Paynter have proposed a similar hypothesis in their study on superhydrophobic silver coatings on copper using FAS-17 molecules in a one-step process (12). The Si 2p peak can be resolved into two components with binding energies of 101.6 and 99.2 eV. The peak at 101.6 eV is assigned to the bonding of Si to O in the FAS molecules and the peak at 99.2 eV is assigned to the Si–C bonds found in the FAS molecules. The binding energy of the Al 2p peak is found to be 74.2 eV which is assigned to $\text{O}-\text{Al}-\text{O}$ (Al_2O_3) bonding (16, 17).

The as-received aluminum surface with an rms roughness of $1.7 \pm 0.2 \mu\text{m}$ provided a water contact angle of $73 \pm 3^\circ$. Following treatment with 0.1 M NaOH, without FAS-17, the roughness increased to $6 \pm 0.5 \mu\text{m}$ providing a slightly higher water contact angle of $88 \pm 10^\circ$. However, when the aluminum surfaces were immersed in 0.1 M NaOH contain-

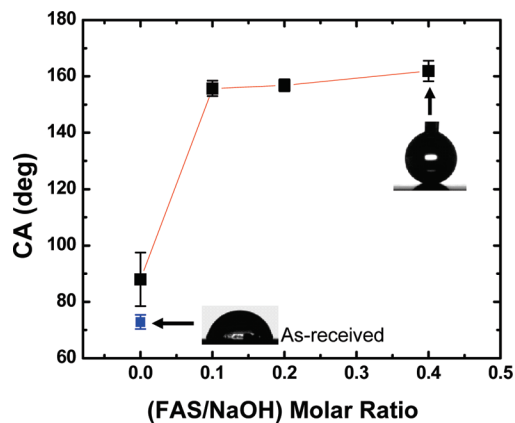


FIGURE 3. Water contact angle measured on aluminum surfaces treated with different FAS-17 concentrations.

ing FAS-17 at different F/OH ratios, the water contact angles were found to slightly increase, although not significantly, as shown in Figure 3. Water contact angles on surfaces treated with F/OH ratios of 0.1 and 0.2 were found to be similar, with values of $156 \pm 3^\circ$ and $157 \pm 2^\circ$, respectively. With further increase in the FAS-17 content in the NaOH solution, with a F/OH ratio of 0.4, a very high water contact angle of $162 \pm 4^\circ$ was obtained. The water contact angle hysteresis of the surfaces treated with F/OH ratios of 0.1, 0.2, and 0.4 were found to be 7 ± 1 , 5 ± 1 , and $4 \pm 0.4^\circ$, respectively. We have previously reported similar high contact angles and low contact angle hystereses on various surfaces produced using two-step processes (8–10, 12). Sarkar et al., reported a water contact angle of $164 \pm 3^\circ$ and hysteresis of $2.5 \pm 1.5^\circ$ via a two-step process on chemically etched aluminum surfaces coated with rf-sputtered Teflon (9). Song and Shen reported a contact angle of 150° on aluminum sheets exhibiting a petal-like structure claiming a one-step process (13). However, these authors obtained the flaky petal-like microstructure by immersion in a 0.5 M $\text{NH}_2(\text{CH}_2)_6\text{NH}_2$ solution, followed by passivation using perfluorodecyltriethoxysilane (PDES), hence following a traditional two-step procedure. In the present study, a water contact angle as high as $\sim 162^\circ$ with a contact angle hysteresis as low as $\sim 4^\circ$ have been obtained using a one-step procedure where the creation of a surface roughness and the lowering of the surface energy takes place at the same time.

This easy and effective one-step process of making aluminum surfaces superhydrophobic may find applications in the aluminum industry where corrosion is of concern, in addition to its potential for easily producing self-cleaning, antifriction and antiwear materials with improved surface properties. Studies point out that the use of superhydrophobic surfaces can inhibit corrosion on metal surfaces, poten-

tially preventing corrosion-induced damage and protecting the surface aesthetics (14).

CONCLUSIONS

In summary, highly superhydrophobic aluminum alloy surfaces have been fabricated via a very simple one-step process by immersing the substrates in a solution containing NaOH and FAS-17 molecules. A water contact angle as high as $\sim 162^\circ$ and a contact angle hysteresis as low as $\sim 4^\circ$ was obtained on the treated surfaces. SEM analysis confirmed the creation of surface roughness and XPS analysis confirmed the presence of the low-surface-energy fluorinated components. The method, itself being very simple and effective, may find its potential applications where problems such as corrosion and other humidity and moisture related concerns are an issue.

Acknowledgment. We acknowledge the financial support provided by the Natural Sciences and Engineering Research Council of Canada (NSERC). We also thank Dr. Danick Gallant of Aluminum Technology Centre, National Research Council of Canada (ATC-NRC) for providing access to contact angle measurements.

Supporting Information Available: Survey spectra acquired from the aluminum surface treated with F/OH ratio of 0.4 and the XPS high-resolution spectra of O 1s, Si 2p, and Al 2p. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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AM100563U