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Fabrication of patterned surfaces that exhibit variable wettability ranging from superhydrophobicity to high hydrophilicity by laser irradiation

Changwoo Lee[a], Handong Cho[a], Dongseob Kim[b], Woonbong Hwang[a,*]

[a] Department of Mechanical Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Gyeongbuk, Republic of Korea
[b] Graduate School of Engineering Mastership, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Gyeongbuk, Republic of Korea

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ABSTRACT

We present a simple method for fabricating patterned surfaces that exhibit different wettabilities in different areas using laser machining. This process can be extended to form complex and large patterns. The first step is the preparation of a superhydrophobic base surface on the aluminum specimen through formation of hierarchical micro- and nanostructures and coating of a self-assembled monolayer. This base surface is then patterned using a laser, which is moved along the surface using a computerized routing system. It was found that the surface hierarchical structures melted to a greater degree with an increase in the laser power used. However, with increases in the laser power, the degree of melting as well as the melted area increased, causing the wettability of the surface to change drastically and making the surface more hydrophilic. In addition, new crumb-like nanostructures were formed for high laser powers, which made the surface rougher and also increased its hydrophilicity. Further, when the rate at which the laser was moved across the machined surface was increased, the contact angle of the irradiated surface decreased for the same laser power. Finally, complex patterns, including stripes and circles, having different wettabilities in different area could be successfully fabricated.

1. Introduction

The contact angle (CA) of a surface is determined by the equilibrium of the forces between the solid, gas, and liquid phases at the three-phase contact line. These forces, in turn, are affected by the surface roughness of the surface and the surface tension of material [1,2]. Surfaces having high and low wettabilities can be fabricated by various methods [3–6]. For instance, surfaces can be tuned superhydrophobic and superhydrophilic (i.e., their CA can be made greater than 150° and almost 0°, respectively) [6,7]. In addition, special structures such as re-entrant (i.e., those with surfaces having concave topographic features) and overhanging ones [8–10] can be fabricated on surfaces to make them superoleophobic with respect to low-surface-energy liquids [11,12]. Among other benefits, these characteristics can help prevent fouling [13–15] and corrosion [16,17], reduce fluid resistance [18–20], and also retard fogging [21,22]. Further, patterned surfaces having different wettabilities are useful in a greater number of applications than surfaces that exhibit just one type of wettability. Some of these applications are water gathering [23,24], microfluid control [25–27], and cell culture [28].

Although such patterned surface can be fabricated by various methods such as plasma-assisted chemical modification [23], photolithography [27–30], sol–gel techniques [25,26], surface-structure modification [31–33], and printing techniques [34,35], these conventional methods involve delicate and time-consuming processes, which are usually expensive and complex. In addition, the area that can be patterned using these techniques is restricted to the size of specimen wafer. Therefore, it is necessary to develop a simple method for fabrication large-area patterned surfaces having different wettabilities.

Recently, several methods have been reported for turning aluminum surfaces superhydrophobic as such surfaces are widely used in industry. These include the anodization of aluminum after a low-plasma treatment [36], dislocation-selective chemical etching of aluminum [37], chemical etching of aluminum by immersing it in sodium hydroxide [38], anodization of aluminum surfaces that have a forest of alumina nanowires present on them [39], and alkali-based surface modification of aluminum [40].

Herein, we report the fabrication of patterned surfaces with different wettabilities. A base surface was first prepared by the chemical etching [37], and alkali-based modification of a specimen of aluminum [40]. Then, a coating of a self-assembled monolayer

* Corresponding author. Tel.: +82 54 279 2174; fax: +82 54 279 5899.
E-mail addresses: hirundo@postech.ac.kr (C. Lee), hyvaa@postech.ac.kr (H. Cho), yusae@postech.ac.kr (D. Kim), whwang@postech.ac.kr (W. Hwang).

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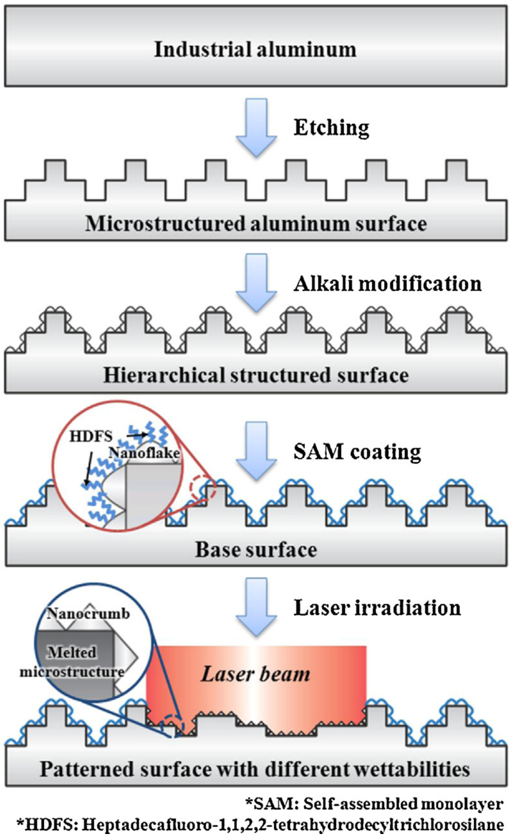

Fig. 1. Process for fabrication a patterned surface with different wettabilities.

(SAM) was formed on the base surface this yielded a large surface having uniform wettability. Finally, this coated surface was patterned by laser irradiation, with the laser being moved around the surface to be patterned using computerized routing system. Although there were several methods to use laser [41–44] for controlling wettability of the surface, the role of laser was not to fabricate patterned surfaces that exhibit different wettabilities in different areas but to make micro structure on the surface.

2. Experimental details

Fig. 1 shows a schematic of the process for fabricating the patterned surface. The process consists of two main steps: the fabrication of a superhydrophobic base surface and the formation of patterns on this base surface. The specimens used for forming the patterned surfaces were of industrial aluminum. First, the aluminum specimen was immerged in 0.5 M NaOH at room temperature to remove the oxide layer and any oil present on its surface. Then, its surface was etched in a 1 M HCl solution at 80 °C for 2 min to form a microscaled structure. Next, the aluminum specimen with the microstructured surface was immerged in an NaOH solution (0.5 M, room temperature) for 10 s to form a nanoscaled structure on its surface. Then, the aluminum specimen was immerged in deionized (DI) water at 95° C for 5 min in order to be stabilized. The thus-formed surface was superhydophilic before being coated with the SAM. The hierarchically structured surface of the aluminum specimen was then coated with a self-assembled monolayer (SAM) of heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilane (HDFS, Gelest Inc.). The aluminum specimen was dipped in an HDFS solution containing n-hexane (volumetric ratio of 1000:1) for 10 min. The specimen was then washed with DI water and dried in an oven at 105 °C for 1 h. The coated specimen exhibited superhydrophobicity; The CA of the base surface is 164.4°.

In the second step, which involves the patterning of the base superhydrophobic surface by laser machining, the base aluminum surface was irradiated with a laser. This increases the temperature of the surface, and the surface is damaged owing to the high thermal energy. As a result of the laser irradiation, the surface melts, and a new nanostructure that is different from the previous nanostructure formed by alkali-based modification process starts to form on the melted surface. The type of nanostructure formed depended on the laser power used. In addition, C–F bond in fluoroalkyl group is disappeared at 500 °C resulting in loss of hydrophobicity [45].

An industrial laser system with computer numerical control (CNC) (HLM49, Hanter Technology Co., Ltd.), which consisted of a laser and a computerized routing system, was used for patterning. The maximum power of the laser is 200 W (radio frequency type) and its maximum machining speed was 300 mm/s. The width of the laser beam used was 250 μm, and the focal length of the lens used was 127 mm. The working area of the specimen was 1300 × 2500 mm. Both the intensity of the laser and rate at which the beam could be moved were controllable.

A surface analyzer (SmartDrop, Femtofab) was used to measure the contact angles for the patterned surfaces through the sessile drop method. The contact angle was measured at a minimum of five different areas for each specimen. The measurements were made using a 3 μl droplet of DI water at room temperature. Scanning electron microscopy (SEM) (JSM-7401FEM-SEM, JEOL Ltd.) was used to investigate the surface morphologies of the patterned specimens.

3. Results and discussion

Fig. 2 shows SEM images of the microstructures of the aluminum specimens after etching with HCl as well as SEM images of the nanostructures of the specimens after their surfaces had been modified with NaOH. In the images in Fig. 2(a) and (b), a number of pits that form labyrinth-like structure can be seen. These pits were formed owing to dislocation defects produced by the attacks on preferential sites having relatively high energy by the dislocation etchant. The morphology seen in the images is similar to that reported by Qian et al. [37]; the fact that the density of pits is greater and that they are more closely packed is because the specimens were etched for a long period. A layer of flake-like aluminum hydroxide with smooth corner can be seen on the microstructured surface in Fig. 2(c) and (d). This morphology is similar to nanostructure reported by Cho et al. [40], while making allowance for the fact that the specimens were immersed in the NaOH solution at a lower temperature and for a shorter period. It should be noted that aluminum hydroxide was present in form of gibbsite in the layer [46].

Submicron-scaled structures existed on the aluminum surface after it was chemically etched, making the surface rough enough to exhibit superhydrophobicity after being coated with the SAM. However, the nanostructures formed by the alkali-based treatment further guaranteed that the surface would be superhydrophobic owing to the increase in the surface area and the formation of covalent bonds between the silanol groups of HDFS and the hydroxyl groups of the aluminum hydroxide present in the form of nanoflakes [47]. After being coated with the HDFS SAM, the CA of the base surface was 164.4°; this was indicative of superhydrophobicity.

Fig. 3 shows SEM images of surfaces irradiated with the laser at 10% and 20% of the maximum power (200 W); the rate at which