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Fabrication of a super-hydrophobic surface on metal using laser ablation and electrodeposition

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ABSTRACT

In this research, the fabrication process of a super-hydrophobic metallic surface using laser ablation and electrodeposition was investigated. Re-entrant structure and surface roughness play an important role in forming a super-hydrophobic surface on intrinsically hydrophilic material. A micro pillar array with a re-entrant structure of copper on stainless steel was fabricated through a sequential process of laser ablation, insulating, mechanical polishing and electrodeposition. Spacing of the micro pillars in the array played a major role in the structure hydrophobicity that was confirmed by measuring the water contact angle. Surface morphology changed relative to the parameters of the laser ablation process and electrodeposition process. Under a gradual increase in current density during the electrodeposition process, surface morphology roughness was maximized for fabricating a super-hydrophobic surface. Finally, the super-hydrophobic surface was successfully fabricated on metal.

1. Introduction

Super-hydrophobic surfaces have been investigated by numerous researchers because of potential applications in self-cleaning, fog-resistance, drag reduction in microfluidics and prevention of corrosion [1]. Two fabrication methods for creating super-hydrophobic surfaces have been developed. In the case of hydrophobic material, high surface roughness can amplify the hydrophobicity of the surface. In the case of hydrophilic material, surface coating that lowers surface energy is needed because roughening the surface makes it more hydrophilic. However, a surface coating of chemical material creates an aging effect. Aging in air leads to a hydrophobic surface, which differs from an untreated surface, both in surface composition and in wetting behavior [2]. Therefore, a durable super-hydrophobic surface should be made up of several physical structures and exclude chemical treatment. Re-entrant structure, such as a micro-hoodoo, mushroom-like topography is well known for its liquid repellent property. In this structure, net traction force of a liquid droplet is upward because of its re-entrant angle between the top surface and side wall of the structure. It has been used in super-oleophobicity due to the low surface tension of oil compared to water [3,4]. Therefore, several studies have been conducted on the super-hydrophobicity on hydrophilic surfaces [5,6]. However, these studies have been at a disadvantage of using a fabrication process that consists of a wafer-based process, which restricts the working environment.

Many attempts have been made to achieve a robust super-hydrophobic surface on metal [7–10]. A physical structure of micro- and nano-sized rough morphology was fabricated using micro-fabrication techniques, such as laser ablation, anodizing, sandblasting and electrochemical etching. Subsequently, the surface energy of the roughened surface was reduced through chemical treatment. Nonetheless, these methods are still subjected to aging problems resulting from the applied chemical treatment.

In order to overcome the drawbacks and enhance the robustness of a super-hydrophobic surface, Bae et al. present a direct, one-step method for fabricating a dual-scale super-hydrophobic metallic surface using wire electrical discharge machining [11]. A micro scale sinusoidal pattern with a wavelength in hundredths of a micrometer and secondary roughness in the form of microcraters was fabricated using wire electrical discharge machining. However, the material used was Al 7075 alloy (duralumin), intrinsically hydrophobic. For these reasons, this fabrication method cannot be used with other metals that are intrinsically hydrophilic.

In the present research, a micro-fabrication process that integrates a laser ablation using a nanosecond pulsed fiber laser and an electrodeposition is introduced to obtain a hydrophobic metallic structure. The fabrication process can be performed in a general working environment, in contrast to other fabrication methods for a re-entrant structure. In addition, a fabricated metallic structure has greater durability against heat and time lapse compared to a polymer-based structure and a chemical treatment to lower the

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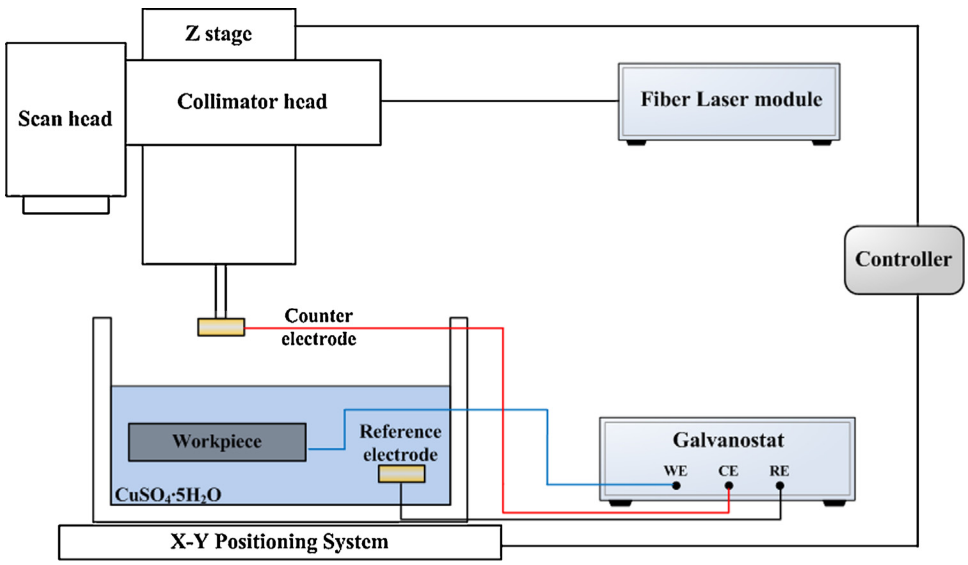

Fig. 1. Schematic of experimental setup for laser ablation and electrodeposition.

surface energy. Using the proposed process, micro pillar arrays with re-entrant structures were fabricated at different micro pillar spacing and surface morphology of the deposited material. Further, the hydrophobicity of the fabricated surface was evaluated with respect to the water contact angle of deionized water droplets. Using this fabrication process, it is possible to obtain a super-hydrophobic surface on hydrophilic metal materials. In addition, this process is expected to broaden the practical application field of super-hydrophobicity that has been limited to some types of films for self-cleaning and preventing the pollution. The super-hydrophobic metallic structure without surface treatments can be applied to many industrial fields by its electrical and thermal properties.

2. Experimental setup

The experimental setup for the fabrication process consists of a pulsed laser system for micro structuring and an electrodeposition system for re-entrant and surface structuring as shown in Fig. 1. The micro-patterned surface of stainless steel was produced through laser ablation using a Yb-doped pulsed fiber laser (IPG photonics, YLP-C series) with a wavelength of 1064 nm and a pulse length of 100 ns at repetition rates ranging from 20 kHz to 80 kHz. Further, the cathodic deposition of copper on stainless steel was performed in an electrochemical cell. To control the current during electrodeposition, galvanostat (potentiostat/galvanostat model 263A from AMETEK) was used. A stainless steel (AISI 304) plate with a thickness of 500 μm was used as a workpiece. The counter and reference electrodes were 99.9% copper rods. The electrolyte for the copper electrodeposition was an aqueous solution of 0.5 M copper sulfate pentahydrate and 0.5 M sulfuric acid. The characteristics of the fabricated structure were studied using a scanning electron microscope (SEM) and contact angle analyzer (Phoenix 150 from S-EO) with 3 μl pendant drop of deionized water.

3. Principle of hydrophobic re-entrant structure

The re-entrant and hierarchical structures are two important elements required to achieve hydrophobicity. The re-entrant structure is especially indispensable for its water repellent property with intrinsically hydrophilic material. Therefore, effective manufacturing of a re-entrant structure is the main goal of the fabrication process. Fig. 2 shows the re-entrant structure and its principle of water repellency [3,4]. Fig. 2(a) and (b) show the schematics of wetting on different physical structures that have the same chemical property. The re-entrant structure is a surface with concave topographic features where the local texture angle ψ is smaller than 90°, as shown in Fig. 2(b). If the contact angle θ of a hypothetical liquid is smaller than local texture angle ψ, the structure is considered to be fully wetted because the net traction force on the liquid–vapor interface is directed downward, as shown in Fig. 2(a). In the case of a re-entrant structure, shown in Fig. 2(b), the structure plays a role in supporting the formation of a composite interface because the net traction force is directed upward. Many researchers have investigated similar kinds of surface structures for the large apparent contact angles [5,6,12].

The micro–nano hierarchical structure is well known for its advantages in fabricating a super-hydrophobic surface. Super-hydrophobic surfaces should be capable of forming a composite solid–liquid–air interface to achieve a large water contact angle. A hierarchical structure makes it possible for a greater composite interface that results in decreased contact area between the liquid droplet and the solid. In addition, the hierarchical structure can prevent the transformation of the composite interface into a homogeneous interface from external factors such as perturbation and the scale of droplets [13]. In this research, a hierarchical structure was fabricated from a micro structure through laser ablation and a sub-micro structure with electrodeposition.

4. Fabrication process for re-entrant structure

The fabrication method of a metallic re-entrant structure requires the sequential process of laser ablation, insulating, mechanical polishing and electrodeposition. Its schematic process is shown in Fig. 3. Primarily, a nanosecond pulsed laser that has a high ablation rate is used to machine a micro structure workpiece. Subsequently, insulating material, such as enamel, is spread on the fabricated area. After insulating, the insulating material applied on the top of the micro structure is eliminated by additional mechanical polishing. The re-entrant structure is electrochemically deposited on the area exposed by polishing. Finally, insulating material is removed by ultrasonic cleaning with acetone. This sequential process can fabricate the metallic re-entrant structure.