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A facile fabrication method for corrosion-resistant micro/nanostructures on stainless steel surfaces with tunable wettability

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ABSTRACT

Superhydrophilic surfaces were fabricated on stainless steel surfaces via simple etching and oxidation processes and were modified by a self-assembled monolayer to provide superhydrophobic surfaces. The micro/nanostructure and reconstructed passivation layer of the stainless steel surfaces exhibited good mechanical durability and long-term stability. The corrosion resistance of the surfaces was investigated using sea water. The test results indicate that the reconstructed passivation layer of the surfaces provides excellent corrosion resistivity. The successful fabrication of large-area superhydrophilic/superhydrophobic surfaces offers the possibility of providing stainless steel surfaces with unique wetting characteristics for various industrial applications.

Stainless steel, originally known as rustless steel, is one of the most widely used steel alloys containing chromium. Its superior properties, such as its excellent mechanical strength and corrosion resistance facilitate a wide range of applications, including cookware, major appliances, construction, surgical instruments, automotive parts, and aerospace engineering. The attractive properties of stainless steel arise from its elemental compositions and phases of metal. The corrosion resistance of stainless steel is attributable to a passivation layer of chromium oxide on the surface.

Recently, in order to increase the benefits that stainless steel offers in the industrial applications, special features have been developed, including self-cleaning [1,2] anti-fogging [3], anti-icing [4], cell adhesion [5], drag reduction [6], water harvesting [7], and oil/water separation [8]. Surface characteristics related to strong attraction and repulsion of water, termed superhydrophilicity and superhydrophobicity, respectively, have been developed to obtain these special benefits from stainless steel. Suggested methods for fabrication of superhydrophilic and superhydrophobic surfaces on stainless steel have been based on femtosecond laser techniques [9], electrochemical anodization [10], the sol–gel method [11], and crystallization [12]. However, the method for fabricating superhydrophobic and superhydrophilic surfaces using a femtosecond laser is not sufficiently scalable, because of the costly specialized setup required and because the method is a projective process that is difficult to apply to a three-dimensional surface. Other methods that involve adding another material to the surface result in low durability because of the low bonding force with the surface. Methods that generate a nanostructure directly on the stainless steel material, such as etching processes [13,14], must be considered to produce stainless steel surfaces with the desired inherent mechanical properties, unlike surfaces produced through deposition of particles or by chemical reaction. Furthermore, specific micro/nanostructures must be considered to obtain superhydrophilic and superhydrophobic surfaces on stainless steel.

Yu et al. used a strong etchant mixture of acid to achieve the necessary surface roughness and a fluorosilane coating on the surface [13]. Although their work indicated that this etching process can be used to produce a superhydrophobic surface on stainless steel, their work did not involve a process for reconstruction of the passivation layer of the stainless steel. The passivation layer of stainless steel plays an important role in corrosion resistance, so reconstruction of the passivation layer must be considered, because the etching process removes the passivation layer and exposes the unstable surface of the stainless steel. Li et al. used an etching process involving hydrofluoric acid and hydrophobic film deposition [14]. Although they reported the dependence of the observed surface properties on the etching parameters and ensured that the surface inhibited corrosion, hydrofluoric acid changes the chemical composition of a stainless steel surface, and a 100-nm hydrophobic polymer coating applied to stainless steel produced a micro/nanostructure that was weakly bonded to the surface and could be easily detached. Previous studies have not addressed the production of superhydrophilic stainless steel surfaces because of the deficient micro/nanostructures of such surfaces.

In this paper, we present a simple method for fabricating both superhydrophilic and superhydrophobic surfaces on stainless steel. Chemical etching and oxidation are used to produce the required surface micro/nanostructures and passivation layer, and the fabricated surface displays good superhydrophilicity. Superhydrophilic surfaces

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are easily changed to superhydrophobic surfaces by a self-assembled monolayer coating. The chemical composition and corrosion resistance of the nanostructured stainless steel surfaces were investigated using X-ray photoelectron spectroscopy (XPS; ESCALAB250, VG Scientific), potentiodynamic polarization, test and simple corrosion test.

Fig. 1a shows the fabrication process for a micro/nanostructured stainless steel surface. The process consists of serial dipping at room temperature, and so stainless steel of any size can be easily fabricated for superhydrophilicity. In this study, 304 stainless steel (iron with 18% chromium and 8% nickel) was used and etched for 6 h in a 40% ferric chloride solution to produce an unpassivated, microstructured surface. The passivation layer of the stainless steel surface was removed by the etching solution. After removal of the passivation layer, the surface was bare, with exposed grain boundaries. The etching solution attacked the weak grain boundary first and affected the entire surface gradually, so that a sub-micron structure was developed, based on the crystal orientation. During the process, the etching residue from the stainless steel covered the entire surface. The lump structure and cracking of the remaining residue were examined using field-emission scanning electron microscopy (FE-SEM; see Fig. 1b(i)). The etched surface was barely visible between the cracks of the lump structure, and so a brush was used to remove any remaining residue and facilitate examination of the etched surface. An FE-SEM image of the etched surface, showing the grain-oriented microstructure, is shown in Fig. 1b(ii). Because the etching residue prevents spontaneous oxidation of the bare surface during exposure to air and cleaning by water, the specimen was cleaned using deionized water for a few seconds under low pressure after the etching process. After cleaning, the specimen was oxidized for 1 h in 35% hydrogen peroxide without drying to reduce the native oxidation. The oxidation reaction was monitored by observing the formation of bubbles, and, during the oxidation, the etching residue was separated from the surface by the bubbles. After full oxidation, a nano-embossed structure of metal oxide is generated, and a hierarchical micro/nanostructure is created (see Fig. 1b(iii)). The insets in Fig. 1 show the color of the specimen's surface, which reflects the structure and chemical nature of the stainless steel surface.

The chemical state was examined to verify the chemical stability of the micro/nanostructure of the stainless steel surface. XPS (ESCALAB250, VG scientific) analyses were conducted on bare, etched, and oxidized surfaces. Fig. 2(a), which shows the XPS survey spectra of the specimens, displays spectral peaks for the elemental compositions. Many impurities disappeared after the etching process, and the oxide peak significantly increased after oxidation of the etched specimen. The chromium and iron peaks are evident for all specimens. The surfaces were attacked by the etching solution and, therefore, the intensities of the elemental metal and metal oxide peaks decreased (see Fig. 2(b)). After the oxidation process, peaks occurred at higher binding energies owing to oxidation of the metal (Fe: 707.2 eV). These results indicate that the surface was fully oxidized and well-passivated.

A self-assembled monolayer (SAM) was used to fabricate a superhydrophobic stainless steel surface to change the inherent surface energy of the stainless steel. A dried specimen was placed in heptadecafluoro-1,1,2,2-tetrahydrodecyl trichlorosilane with n-hexane (volumetric ratio 1:1000) for 2 h. After the reaction and coating processes were completed, the stainless steel surface was rinsed with n-hexane and dried at room temperature. SAM coatings known not to change the structures of surfaces [15,16], so the micro/nanostructures of the stainless steel surface had to be accurately characterized. Static contact angles were measured using deionized water and a surface analyzer (DSA-100 and Smart Drop) to verify the change in the wettability of the surface, from superhydrophilicity to superhydrophobicity. A sessile drop method was used in these observations, and five different positions were checked on each specimen using a 5-μl droplet. Following etching and oxidation, the stainless steel surface exhibited good superhydrophilicity, with a near zero contact angle and instantaneous spreading of a droplet (see support information S1). This degree of wettability indicates that the micro/nanostructure amplifies the inherent hydrophilicity of the metal surface, according to Wenzel's equation [17,18]. Application of the SAM coating changed the surface energy, and the surface exhibited superhydrophobicity, with a contact angle of 158.3° and roll off angle of 5.1° (see S2). The fabrication method, which consists of serial dipping, is applicable to large stainless steel specimens. Superhydrophilic surfaces were fabricated on thin sheets

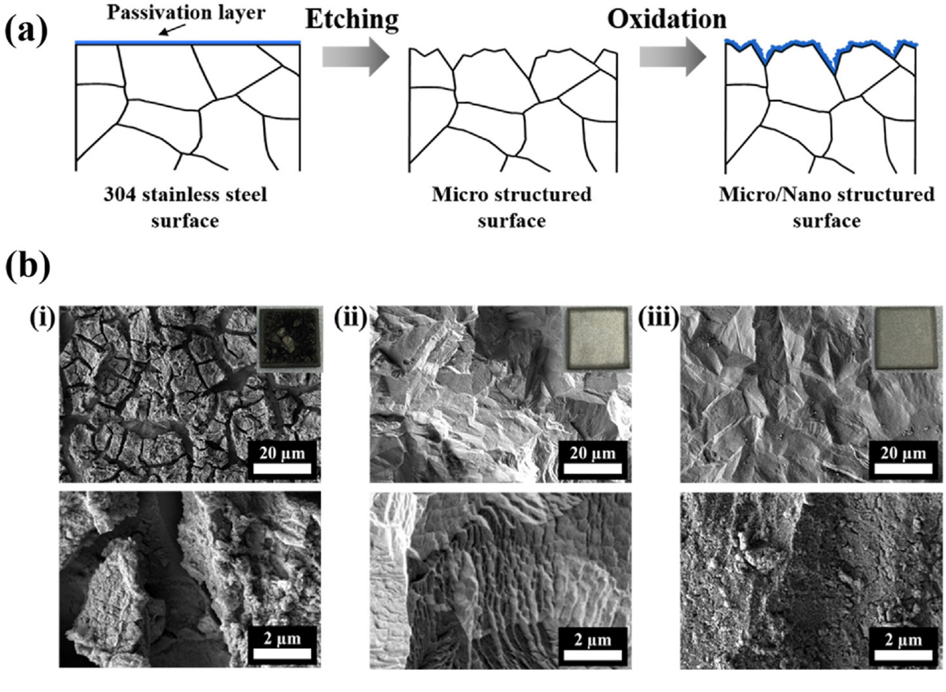

Fig. 1. Micro/nanostructure produced on stainless steel surface. (a) Scheme of the micro/nanostructure fabrication process on the stainless steel. (b) FE-SEM images of stainless steel specimens after etching and oxidation processes. The insets show the color of the stainless steel surface according to process step ((i): an etched surface with the etching residue, (ii): an etched surface, (iii): an etched and oxidized surface).