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Thermal stability of the structural features in the superhydrophobic boehmite films on austenitic stainless steels

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Abstract

Boehmite thin film with 50–100 nm surface flake structure has been synthesized on AISI 316 type austenitic stainless steel by immersing boehmite gel film into boiling water. When further coated with hydrolyzed (heptadecafluoro-1,1,2,2-tetrahydrodecyl) trimethoxysilane (FAS), the boehmite film becomes superhydrophobic with a contact angle for water of 152°. The superhydrophobic property results from both the nanoscale surface flake structure and the low surface energy of the FAS top layer. The topography of such film was revealed by atomic force microscope (AFM) and a set of roughness parameters of such film was discussed. The degradation of superhydrophobicity of the surface was studied as a function of the heat-treatment temperatures. Below 600 °C, the surface remained to be superhydrophobic with the FAS top layer. Above 700 °C, the surface was not superhydrophobic anymore due to a gradual loss in surface roughness which was revealed by field emission scanning electron microscope (FESEM). A phase change from boehmite to γ-Al_2O_3 occurred during the heat-treatments from 700 to 900 °C which was studied by the selected area electron diffraction (SAED) patterns from the transmission electron microscope (TEM) measurement.

Keywords: Superhydrophobic; Sol–gel technique; Roughness parameters; Transmission electron microscope; Selected area electron diffraction

1. Introduction

Currently, a surface with a contact angle for water greater than 150°, called superhydrophobic surface, has been attracted more and more interest in both industry and research [1,2]. Due to the limited contact area between the solid surface and water, chemical reactions or bond formation with water are limited on a superhydrophobic surface. Therefore, various phenomena such as adherence of snow, oxidation and electrical conduction are expected to decrease on such a surface [3]. Furthermore, superhydrophobic property facilitates the removal of particulate depositions such as dust and results in purification of the surface through rain, fog, or dew (Lotus effect), which is called self-cleaning or easy-to-clean property [4]. The use of detergents is not necessary for such a surface, and thus the surface is environmentally friendly. Self-cleaning or easy-to-clean surface would be of great benefit for human daily life.

To obtain superhydrophobic surfaces, surface energy and surface roughness are two dominant factors. When surface energy is lowered, the superhydrophobic property is enhanced. However, surface energy is an intrinsic property of each material, and the common material with possibly the lowest surface energy to the authors' knowledge (6.7 mJ/m^2 for a surface with regularly aligned closed-hexagonal-packed –CF_3 groups) gives a contact angle for water of only around 120° on a flat surface [5,6]. Therefore, surface roughening must be combined with low surface energy to produce a superhydrophobic surface. By lowering surface energy with a (heptadecafluoro-1,1,2,2-tetrahydrodecyl) trimethoxysilane (FAS) top layer, a surface with nanoscale surface roughness becomes superhydrophobic with contact angle for water above 150° [7].

Conventionally, superhydrophobic surfaces can be produced in two ways. One is to create roughness on a hydrophobic

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surface (contact angle > 90°), and the other is to coat low surface energy molecules, such as fluoroalkylsilanes on a rough surface [8,9]. Up to now, many methods have been reported on the synthesis of superhydrophobic surfaces [1–3,5–9]. Among these methods, the sol–gel technique is a good option since it can produce thin films on various substrates such as glasses, metals, ceramics, and polymers. The process is cost effective with easy operation. Even multifunctional thin films can be prepared by the sol–gel technique either by coating solid substrates with sol mixtures consisting of various types of starting materials, or by stacking functional layers step by step on solid substrates [10].

As a widely used material, stainless steel has played a very important role in daily life as construction material and as building material for the process industry. Therefore synthesis of self-cleaning or easy-to-clean film on stainless steel is a very practical and beneficial issue. In the present paper, a superhydrophobic boehmite film with 50–100 nm surface flake structure was synthesized on AISI 316 type austenitic stainless steel by the sol–gel technique. To the authors' knowledge, this is the initial report of synthesis of such film on stainless steel. Typically many superhydrophobic surfaces suffer from weak wear resistance. A high temperature treatment would form oxide from hydroxide and remove water, which could improve the mechanical properties and resistance of the surface. For this purpose, thermal stability of such nanoscale surface flake structure was initially studied in this paper to find out the temperature range in which such nanoscale surface structure can be retained so that the surface can remain superhydrophobic. The effect of heat-treatment temperatures to the mechanical properties of such a film will be studied in the future.

2. Experimental

The raw materials are aluminium tri-*sec*-butoxide (denoted as Al (O-*sec*-Bu)$_3$, $C_{12}H_{27}AlO_3 > 97\%$, VWR), isopropyl alcohol (denoted as i-PrOH, $C_3H_7OH > 99\%$, VWR) and ethyl acetoacetate (denoted as EAcAc, $C_6H_{10}O_3 > 98\%$, VWR). Firstly, 3 g Al (O-*sec*-Bu)$_3$ and 30 ml i-PrOH were mixed and stirred at room temperature for 1 h. Then 2 ml EAcAc was introduced, and the solution was stirred for 1 h. After that, the mixture of 1 ml water and 5 ml i-PrOH was added for hydrolysis and with mixing for another 2 h the solution was ready for coating. Similar process can be found in Tadanaga et al.'s work [11]. The substrate in this work was AISI 316 type austenitic stainless steel, which was firstly cleaned in acetone and then in ethanol ultrasonically for 10 min, and finally rinsed with deionized water. After cleaning, spin coating was carried out at 1500 rpm for 20 s. The sample was dried at room temperature under ambient condition for a few minutes, and then heat-treated at 400 °C in air for 15 min to obtain a gel film. After cooling down, the gel film was immersed into boiling water for 10 min, and then dried at room temperature under ambient condition. The surface chemistry of the as-synthesized film was modified by (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trimethoxysilane ($CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$, denoted as FAS, ABCR GmbH & Co. KG, Karlsruhe, Germany). The FAS solution was prepared by mixing 1 ml FAS and 50 ml ethanol for 1 h. Then the film was immersed into the FAS solution for 1 h, followed by heating at 180 °C for 1 h. Then the film was ready for characterizations. To study the thermal stability of the films, post-heat-treatments from 100 to 900 °C for 30 min were carried out before the FAS treatment. After that as a final step, the films were treated with FAS.

Surface morphology was examined with a field emission scanning electron microscope (FESEM, Hitachi S-4800). A thin film (1–2 nm) of Pt/Pd alloy (80/20) was sputtered on the sample to increase conductivity. Surface topography was observed by atomic force microscope (AFM). The AFM images were recorded with a Nanoscope IIIa AFM (Digital Instruments, Santa Barbara, CA). All images (512×512 pixels) were measured in air without filtering. The scanning probe image processor (SPIP, Image Metrology, Denmark) software was used for the roughness analysis of the images [12]. A set of roughness parameters has been developed and standardized for versatile characterization of various surface properties in three dimensions [13]. A more thorough description of the parameters can be found elsewhere [14]. Water contact angles were measured by a system (Pisara, FotoComp Oy, Jyväskylä, Finland), which is composed of a microliter syringe for releasing water droplet and an optical system connected to a computer for data analysis. The water droplet size was 5 μl in the measurements. Droplets were placed at five positions and the average value was accepted as the final contact angle value.

The film is too thin to reveal phase structure by X-ray diffraction (XRD). Therefore, phase transformation of the films during the post-heat-treatments was studied by transmission electron microscope (TEM, Jeol JEM 2010). Selected area electron diffraction (SAED) was used to analyze the phase structure. The TEM samples were prepared in the following way. The stainless steel substrate was pre-thinned mechanically by different SiC grinding papers with grit sizes from 120 to 1200 to a thickness of 0.1 mm. Then disks with diameters of 3 mm were cut from the pre-thinned steel plate by a disc punch (model 310, South Bay Technology Inc.). A small hole was made in the center of the disks by final thinning, which was done by a Tenupol 5 twin jet electrolytic polisher (Struers) using a solution of nitric acid in methanol (1:2) at −50 °C. The films were made on the disks by the same procedures as described aforehand. In this way, the film on the edge area of the central hole is thin enough to be observed in TEM.

3. Results and discussion

The surface morphology of the stainless steel substrate is shown in Fig. 1(a). Grain boundaries can be clearly seen due to the pickling of the stainless steel in the production process. The surface structure of the as-synthesized film consists of 50–100 nm flakes which are evenly distributed, see FESEM images in Figs. 1(b) and (c), which agrees well with the previous studies [7,11,15]. As reported, such a surface structure consists of boehmite, which is probably formed by the process in which