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Effect of heat treating gel films on the formation of superhydrophobic boehmite flaky structures on austenitic stainless steel

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Abstract

The effect of heat treating gel films at different temperatures on the formation of the boehmite flaky structures on AISI 316 type austenitic stainless steel is investigated. After heating at different temperatures, the reactivity of the gel films with boiling water to form boehmite flakes was different, which resulted in different morphologies and different contact angle values after coating with hydrolyzed (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trimethoxysilane (FAS). When the gel film was heat treated from 200 to 600 °C, the resulting contact angle was above 150°, indicating superhydrophobic behavior. However, when the gel film was heat treated below 200 °C as well as at 700 and 800 °C, only some boehmite flakes were formed; when the gel film was heat treated at 900 °C, no boehmite flakes were observed. In these cases the surface roughness is insufficient for the superhydrophobicity. The formation condition of the boehmite flakes by reaction of the gel film with boiling water is also tentatively discussed.

Keywords: A. Films; A. Sol–gel processes; B. Electron microscopy; Superhydrophobic

1. Introduction

Superhydrophobic and self-cleaning properties, demonstrated by lotus leaves (Lotus Effect), have been recognized to be of great technical importance. In lotus leaves, such properties are based on a two-tier (micro and nano) roughness and a low surface energy introduced by surface wax crystals. Air is trapped between water droplet and surface which decreases the contact area between them. The resulting contact angle for water on lotus leaves is up to 170°. Therefore, on such leaves, rain, fog or dew droplets can roll off from the surface and take away the particulate depositions such as dusts, leading to self-cleaning of the surface [1,2]. After Barthlott and Neinhuis' papers about Lotus Effect, lots of research efforts and many experimental methods have been reported to mimic the lotus leaves to produce artificial superhydrophobic and self-cleaning surfaces on bulk materials. Conventionally, the hydrophobicity can be enhanced in two ways: one is to create roughness on a hydrophobic surface (contact angle >90°) [3], and the other is to coat low-surface energy molecules, such as fluoroalkylsilanes on a rough surface [4,5]. Till now, plasma and chemical vapor deposition (CVD) have been commonly reported [6–8]. Lithography [9,10], laser treatment [11] and reactive blending of polymers [12] also work well to prepare superhydrophobic and self-cleaning surfaces. Besides, chemical bath deposition [13], chemical etching on aluminum, copper and zinc substrates [14], sol–gel technique [15], and others [16–21] have also been used. However, most of the above mentioned methods are only suitable for planar surfaces and surfaces of limited size [3]. Moreover, it is difficult to control the formation of the surface structure and sometimes the processing could be complicated and time consuming.

Tadanaga et al. [22] have reported a simple synthesis of transparent superhydrophobic boehmite film on glass substrate by a modified sol–gel technique. In their work, other than the conventional sol–gel technique, they immersed the heat treated gel film into boiling water. The film reacted with boiling water to form boehmite film with 50–100 nm flakes on the surface.

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After coating a (heptadecafluoro-1,1,2,2-tetrahydrodecyl)-trimethoxysilane (FAS) top layer, the surface became superhydrophobic due to the surface roughness from the boehmite flakes and the low surface energy introduced by the FAS top layer. They also reported the effect of the immersing time into the boiling water on the formation of the boehmite flakes and the resulting contact angle values [23]. When a FAS top layer was coated, the contact angle for water was increased with an increase of immersion time, and the film that was immersed for 30 s became superhydrophobic. Unfortunately they did not study the influence of heat treating gel films at different temperatures on the formation of the boehmite flakes and the resulting contact angle values. And they did not discuss the formation condition of the boehmite flakes by immersing the heat treated gel film into boiling water. In this paper, such superhydrophobic films were successfully reproduced on austenitic stainless steel, which gave us a chance to study the effect of the heat treatment temperatures of the gel films on the formation of such superhydrophobic films. Furthermore, the formation condition of the boehmite flakes by reaction of the gel film with boiling water is tentatively discussed. This study helps to understand more about the formation process of such superhydrophobic films.

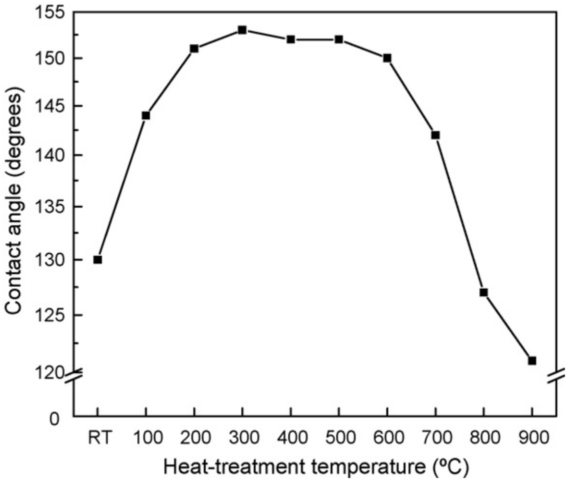

Fig. 1. Contact angles for water of the as-synthesized films (boiling water treated and FAS treated) obtained of the heat treatments from RT to 900 °C for 15 min.

2. Experimental

The sol–gel precursor was prepared by aluminum tri-sec-butoxide (denoted as Al(O-sec-Bu)$_3$, $C_{12}H_{27}AlO_3$ >97%,

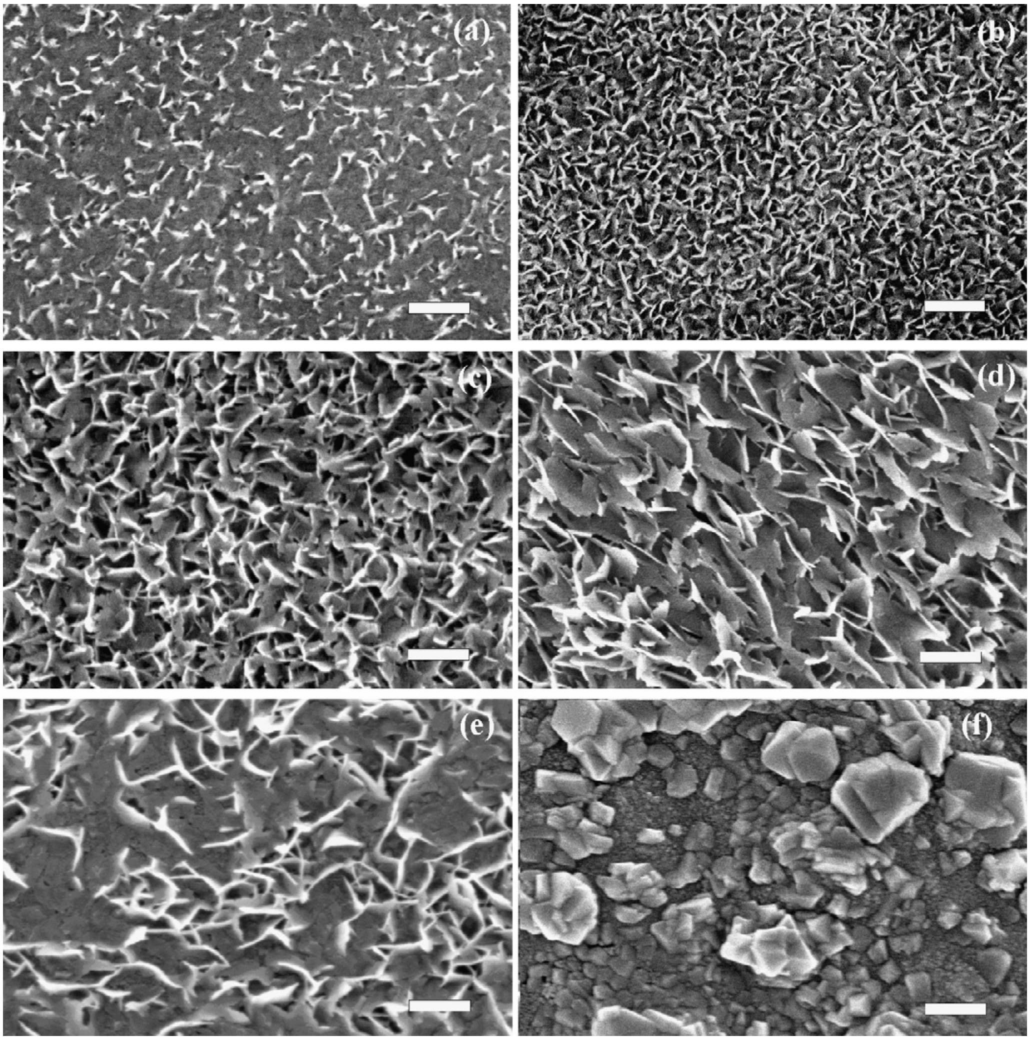

Fig. 2. FESEM surface images of the corresponding films in Fig. 1 at RT (a), 100 °C (b), 400 °C (c), 700 °C (d), 800 °C (e) and 900 °C (f). Bars = 200 nm.

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 (RT) 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. The substrates in this work were AISI 316 type austenitic stainless steels (surface finish 2B), which were firstly cleaned in acetone and then in ethanol ultrasonically for 10 min, and finally rinsed with distilled water. The surface topography of the stainless steel substrate was reported elsewhere [24]. After cleaning, spin coating was carried out at 1500 rpm for 20 s to deposit gel films on the substrates. The gel films were dried at room temperature under ambient condition, and then heat treated from 100 to 900 °C in air for 15 min with a heating and cooling rate of 30 °C/min. After cooling down, the films were immersed into boiling water for 10 min. The surface chemistry of the as-synthesized films were 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 films were immersed into the FAS solution for 1 h, followed by heating at 180 °C for 1 h.

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 contact angle was calculated based on the length and the height of the droplet. Water droplets in size of 5 μl were placed at five positions and the average value was accepted as the final contact angle value. 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. The heat treated gel films were too thin for their phase structures to be revealed by X-ray diffraction (XRD). Therefore, selected area electron diffraction (SAED) from transmission electron microscopy (TEM, JEOL JEM 2010) was used to analyze the phase structure. 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 substrate by a disc punch (model 310, South Bay Technology Inc.). A small hole was made in the center of the steel disk 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 steel disks were dipped into the precursor to form gel films which were dried at RT and then heat treated from 100 to 900 °C for 15 min. After that, the films were immersed into boiling water for 10 min to form boehmite. In this way, the film on the edge area of the central hole was thin enough to be observed in TEM, and more importantly the film was developed to correspond to the actual film structure made on the austenitic stainless steel by spin coating as closely as possible.

3. Results and discussion

Fig. 1 shows the contact angles for water of the as-synthesized films (boiling water treated and FAS treated) obtained of the heat treatments at different temperatures. The contact angle is above 150° between 200 and 600 °C, whereas

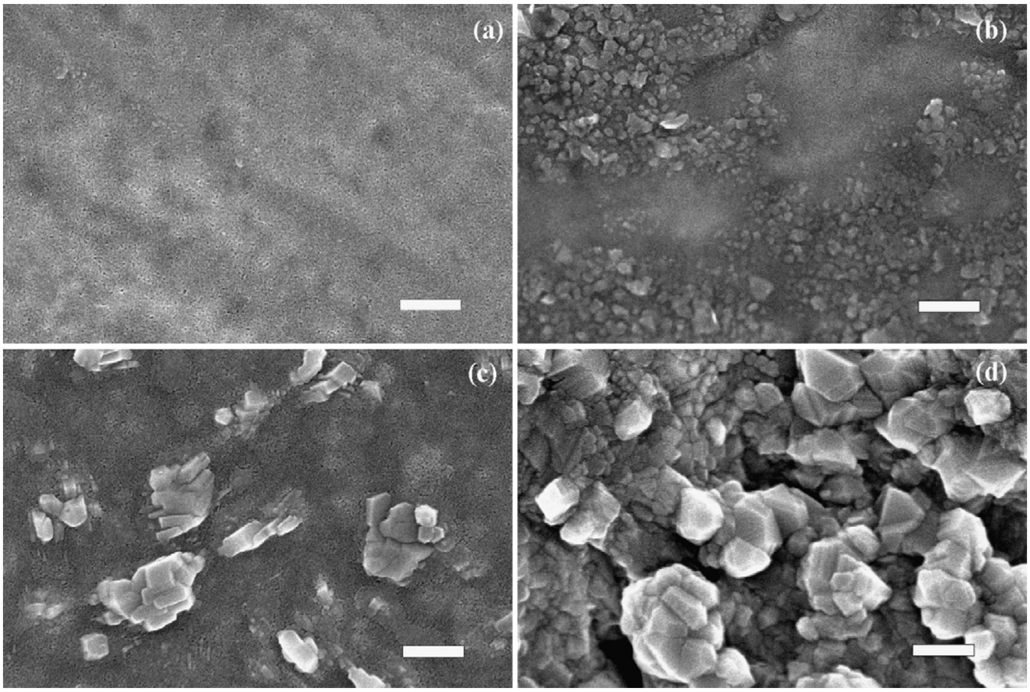

Fig. 3. FESEM surface images of the gel films heat treated at 600 °C (a), 700 °C (b), 800 °C (c) and 900 °C (d) for 15 min before the boiling water treatment. Bars = 200 nm.

the contact angle is 130° at RT, 144° at 100 °C, 142° at 700 °C, 127° at 800 °C, and 121° at 900 °C. As known, surface energy and surface roughness are two dominant factors to obtain superhydrophobic surface. In this study, low surface energy is introduced by the FAS top layer. Since the surface energy is an intrinsic property of each material, the contact angle mainly depends on the surface roughness. Contact angle above 150° indicates surface topography to be in an optimized range to trap enough air which reduces the contact area between the surface and the water droplets. However when the contact angle is under 150°, the surface roughness is not in the optimum range for superhydrophobicity. The FESEM images in Fig. 2 show the morphologies of the corresponding films in Fig. 1. At RT, only part of surface was covered with 50–100 nm boehmite flakes after reaction with boiling water, leading to a contact angle of 130°. At 100 °C, the surface was covered completely with the 50–100 nm boehmite flakes, which gave a higher contact angle of 144°. Between 200 and 600 °C, the flakes in scales of 100–200 nm led to contact angles to be above 150°. A typical surface image of such films is shown in Fig. 2(c). At 700 °C, the surface flakes grew larger and seemed to be more parallel to the substrate, which led to a decrease in surface roughness and a decrease in contact angle to 142°. At 800 °C, flakes of 100–200 nm in size were formed on part of the surface, leading to a further roughness decrease and then a contact angle of 127°. At 900 °C, flakes were not formed on the surface. Instead, some equiaxed crystals were observed which gave the lowest surface roughness and also the lowest contact angle of 121°.

To study the influence of the heat treatment temperature of the gel films on the formation of the boehmite flakes, the heat treated gel films before boiling water treatment were observed by FESEM as comparison. Surface flakes were not observed on all the heat treated gel films, which proved that the surface flakes were formed by reacting with water. The surfaces were flat for the gel films heat treated below 700 °C, with a typical image in Fig. 3(a) in which the gel film was heat treated at 600 °C for 15 min. Particulates are not observed on the surface, but some pores can be seen. However, at 700 °C, some particulates of about 50 nm showed up on the surface. At 800 °C, the particles grew larger to 100–200 nm. At 900 °C, the surface was full of the equiaxed crystals in a scale of about 200 nm. It is supposed that at RT and 100 °C the films were still in the gel state. When the gel films were heat treated from 200 to 600 °C, amorphous and nanocrystalline γ-alumina was formed

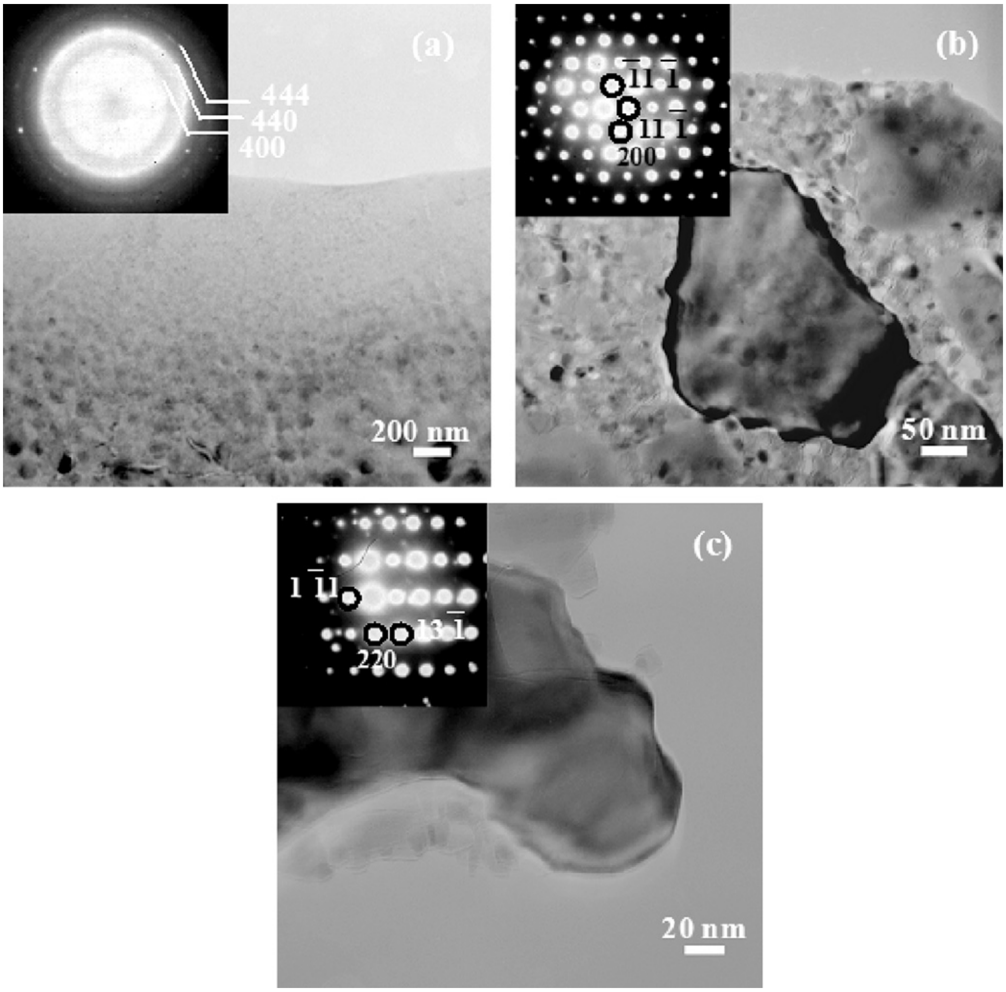

Fig. 4. Typical TEM images of the gel film on the steel disk heat treated at 600 °C (a) and 900 °C (b). The TEM image in (c) was taken after the disk sample in (b) reacted with boiling water. The SAED pattern in (a) was taken from the edge area, and the SAED patterns in (b) and (c) were from the corresponding crystallites on the images. Both SAED patterns were indexed according to γ-alumina with beam directions of [0 1 1] in (b) and [$\bar{1}$ 1 2] in (c).

with the increase of the heat treatment temperatures. As known, even at neutral pH and in the absence of any transition metal ions, γ-alumina is not stable upon contact with water, and will transform back into a hydrated phase [25]. Therefore, boehmite forms on the surface of γ-alumina when the film is immersed into the boiling water. On the other hand, the Al atoms in the boehmite lattice form a deformed octahedron with four oxygen and two hydroxide neighbors. Such octahedron joined by edges results in AlOOH polymeric layers. These layers are held together by hydrogen bonds between the OH^- groups of each octahedron [26]. Therefore boehmite has a preferential growth direction due to the presence of weak hydrogen bonds and interaction between the solvent molecules and the surface OH^- groups via hydrogen bonds [27]. The above explains the formation of boehmite flakes on the surface of amorphous and nanocrystalline γ-alumina which formed from 200 to 600 °C. The TEM study confirms the formation of nanocrystalline γ-alumina, as shown in Fig. 4(a). The disc sample was heat treated at 600 °C for 15 min, and then observed under TEM. The SAED pattern was taken from the edge area of the central hole of the disc. The rings in the SAED pattern reveal the formation of nanocrystalline γ-alumina. The particles in the bottom of the image are from the stainless steel substrate. When the gel films were heat treated at higher temperatures, γ-alumina gets more and more crystallized and the nature of the OH groups on the surface of γ-alumina may become different [28]. Therefore γ-alumina crystals may be difficult to react with water and may need much longer time to react with water to form boehmite flakes. At 800 °C, some γ-alumina crystals showed up, which led to the formation of poorly shaped boehmite flake structure after immersing into boiling water for 10 min. And at 900 °C, the gel film was full of equiaxed γ-alumina crystals which did not react with water with an immersing time of 10 min. This could explain the similarity of the FESEM images in Figs. 2(f) and 3(d). A TEM disc sample was heat treated at 900 °C for 15 min, and then studied under TEM, see Fig. 4(b). Then the disk sample was reacted with boiling water for 10 min, and studied again under TEM, see Fig. 4(c). Flakes were not observed at all under TEM either before or after the water treatment in Fig. 4(b) and (c). The SAED pattern of the gel film heat treated at 900 °C suggests that the crystals are due to γ-alumina with a beam direction of [0 1 1], as shown in Fig. 4(b). The particle size agrees well with the FESEM image in Fig. 3(d). And after the boiling water treatment, the SAED pattern reveals that the crystals remained to be γ-alumina with a beam directions of $[\bar{1}\,1\,2]$ as shown in Fig. 4(c), which could prove that the γ-alumina crystals did not react with water.

4. Conclusions

The influence of heat treating the gel films at different temperatures on the formation of superhydrophobic boehmite flaky thin films on AISI 316 type austenitic stainless steel was studied. When the gel films were heat treated from 200 to 600 °C, the films are superhydrophobic with resulting contact angles above 150°. However, only some boehmite flakes were formed when the gel films were heat treated below 200 °C as well as at 700 and 800 °C; and no boehmite flakes were formed when the gel films were heat treated at 900 °C with resulting contact angles for water less than 150° in all cases. Possibly below 200 °C, the films were still in the gel state. Between 200 and 600 °C, amorphous and nanocrystalline γ-alumina was formed and it reacts with water to form boehmite flakes. However, at 800 °C, some γ-alumina crystals showed up, which led to the formation of poorly shaped boehmite flake structure. Whereas at 900 °C, the gel film constituted of equiaxed γ-alumina crystals, which could not react with water to form boehmite flakes.

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