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The Evaluation of the Structure and Hardness of the Super Water-Repellent Film Including Nano Particles

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Water-repellency is one of the important properties for industry and our life. Water-repellency is determined by the chemical factor (surface energy) and geometric factor (surface structure). In this study, the super water-repellent film showing the water contact angle of about 160° was obtained. The transmittance in the visible wavelength of prepared super water-repellent film was more than 80%. The surface microstructure was controlled by SiO_2 nano particles and the surface sol-gel method, which is the fabrication technique for metal-oxide thin film with the possibility of thickness control with nano scale order. And the super water-repellent film was prepared after water-repellent treatment by *n*-octadecyltrichlorosilane. We described the relationship between the surface microstructure and water-repellency, and evaluated abrasion characteristics of the super water-repellent film.

Key words: water-repellent, nano particle, hardness

1. INTRODUCTION

Wettability of the solid surface is a characteristic property of materials and depends on both the surface energy and the surface structure. Since surface energy is an intrinsic property of each material, controlling the wettability of a solid surface is very difficult. The super hydrophilic TiO_2 surface that shows water contact angle of 0° had been discovered [1-3]. However various industrial products demand not only hydrophilic surface but water-repellent surface.

When the surface energy is lowered, the water-repellency is enhanced. However, even a material with the lowest surface energy ($6.7 mJ/m^2$ for a surface with regularly aligned closest-hexagonal-CF_3 groups) gives a water contact angle of only around 120° [4]. For the fabrication of super water-repellent surfaces or films, the combination of low surface energy and surface roughness is very important [5].

When the roughness increases, the water-repellency increases, whereas the transparency decreases [6-8]. Therefore, precise control of the roughness is required to satisfy both properties. Since the visible light wavelength range is 400-750 nm, the surface roughness for transparent films should be no larger than 100 nm. The hardness of the super water-repellent film is very important for application. But there is few report that described about the hardness of the super water-repellent film.

For the preparation of super water-repellent surfaces, thus the main problem is water-repellency and transparency and hardness. These problem are competitive properties.

On the other hand, there is a useful film fabrication process named a surface sol-gel method [9]. In this method, the ultra-thin film was grown on the basis of dehydration or dealcoholization between metal alkoxide and hydroxyl group of the surface as shown Fig. 1. The film was grown by repeating the following steps: (1) chemical adsorption of metal alkoxide; (2) rinse; (3) hydrolysis of the surface; and (4) drying. The hydroxyl group on the surface of the substrate confined the chemical adsorption with only one cycle of the reaction and this controlled the deposited film thickness with molecular level order precision. In this study, we controlled surface microstructure by the surface sol-gel method and SiO_2 nano particles. And we obtained super water-repellent surface that these microstructure coating by *n*-octadecyltrichlorosilane.

We described relationship between water-repellency and abrasion hardness of prepared film.

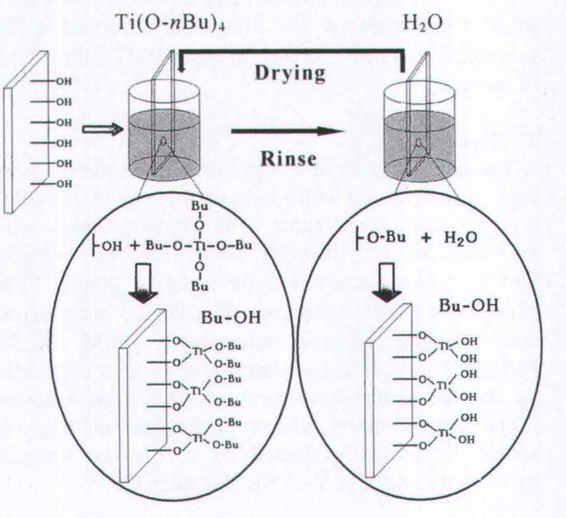


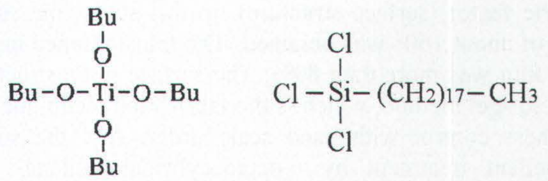
Fig. 1 Schematic illustration of surface sol-gel method of $Ti(O\text{-}nBu)_4$ and water.

2. EXPERIMENTAL METHODS

2.1. Materials

Titanium butoxide [Aldrich., mol. wt. 340.0; denoted as Ti(O-*n*Bu)$_4$] was mixed with 2-propanol [Junsei Chemical Co], concentration of 0.1M solution was prepared as metal alkoxide solution. SiO_2 particles [Japan AEROSIL; Average particle size: 12 nm] was mixed with 18MΩ pure water, concentration of 2 g/L solution was prepared as hydrolysis solution. Slide glass substrate was cleaned by 18MΩ pure water, and etched by KOH solution.

Silane coupling agent, *n*-octadecyltrichlorosilane [$CH_3(CH_2)_{17}SiCl_3$, Tokyo Kasei Kogyo Co ; denoted as OTS] was used as a water-repellent agent. Structural formula of Ti(O-*n*Bu)$_4$ and OTS are shown in Fig. 2.



Titanium Butoxide
Bu: butyl group

n-octadecyltrichlorosilane

Fig. 2 Structural formula of Ti(O-*n*Bu)$_4$ and OTS.

2.2. Preparation of rough surfaces by the surface sol-gel

The slide glass substrate was immersed in 0.1M alkoxide solution of Ti(O-*n*B)$_4$ in 2-propanol, followed by rinsing two successive baths of 2-propanol. The substrate was then immersed in SiO_2 solution, and subjected to the same rinsing procedure. The each of immersion time was 2 minutes.

As this process was 1 cycle, the number of cycles was changed from 0 to 40. And the films were dried at 100℃, for 1 hour in vacuum.

2.3. Water-repellent process

OTS was mixed in Hexane, concentration of 0.4 ml/L solution was prepared. The films were immersed in this solution for 10 min and then dried at 100℃, for 1 hour in vacuum.

2.3. Evaluation

The contact angle of a water droplet on the prepared films was measured with a contact angle meter [CA-DT, Kyowa Interface Science]. The contact angles were measured at five different points for each sample. Surface microstructure was observed by atomic force microscopy [AFM, nanoscope Ⅲa, Digital Instruments] and scanning electron microscope [SEM, XL30, PHILIPS]. The abrasion characteristics were evaluated by the measuring instruments of thin film hardness [Type 18L, Shintou Science Co]. Transmittance of visible light was evaluated by a UV-vis scanning spectrophotometer [UV-3150, Shimadzu Co].

3. RESULTS AND DISCUSSION

3.1. Contact angle measurement

In the case of 0, 10, 20, 30 and 40 cycles, water contact angle were 106°, 111°, 115°, 161° and 159° respectively. The photographs of water droplets of the number of cycles (a) 0, (b) 40 were shown in Fig. 3. In the case of 40 cycles, the shape of the water droplet was almost spherical. The relationship between the water contact angle and the number of cycles was shown in Fig. 4. It was found that between the number of cycles 20 to 30, the water contact angle was changed dramatically. Then in this interval, it was expected that the structural change from water-repellent to super water-repellent.

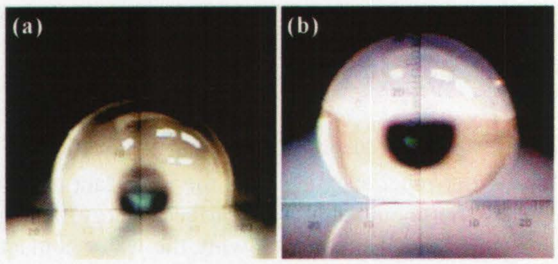


Fig. 3 Photographs of water droplet of the prepared film surfaces with the number of cycles (a) 0, (b) 40.

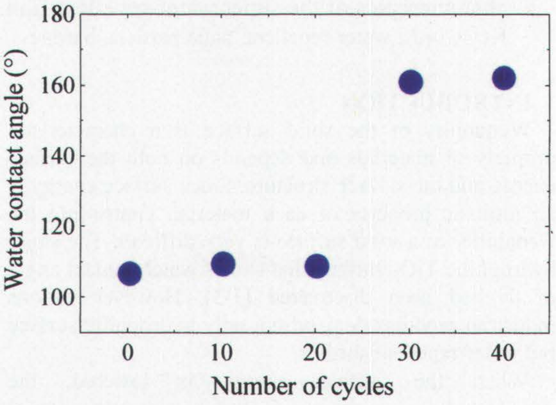


Fig. 4 The relationship between the number of cycles and water contact angle.

3.2. Observation of the prepared film surfaces

SEM images of the prepared film surfaces with the number of cycles (a) 10, (b) 20, (c) 30, (d) 40 were shown in Fig. 5.

As shown in Fig. 5 (a), the film was consisted of island growth. These micrographs revealed that the film surface structure became more roughness as the number of cycles increased. It was found that the prepared film surface of the number of cycles (c) 30, (d) 40 looked to be the surface structure of lotus leaf with combined micro and nano scale concavo-convex structure.

AFM 3D image of the prepared film surface with the number of 40 cycles was shown in Fig. 6. The height of concavo-convex was controlled less than 1 μm. The average roughness of the surface was calculated to be 58 nm from the AFM image.

3.3. Analysis of the surface structure

The cross sections of AFM images with the number of cycles (a) 10, (b) 20, (c) 30, (d) 40 were shown in Fig. 7. All of the surfaces consist of assemblies of needle-like structures. The height of needle increased as the number of cycles increased. In the case of 10 cycles, the height of needle was less than 100 nm. On the other hand, the case of 40 cycles, the height of needle was about 250 nm. And the width of pitch was less than 1 μm. The height of needle revealed about 200 nm as the expression of the super water-repellency at the number of cycles 30, 40.

Bearing analysis of prepared film surfaces with the number of cycles ●10,▲20,■30,◆40 was shown in Fig. 8. Bearing analysis provided a method of plotting and analyzing the distribution of surface height over a sample. It was found that the depth of 200-300 nm was very important for the expression of the super water-repellency. Furthermore, the case of the number of 40 cycles, since the depth of 200-300 nm increased, the surface revealed sliding angle of 1° for 7 mg water droplet.

Characteristic change is carried out from water repellence among 20 to 30 cycles at super water-repellence. Wettability of the solid surface is determined by the chemical factor of surface energy, and the geometric factor of surface concavo-convex structure. Since the same water-repellent processing was carried out by OTS in all films (0, 10, 20, 30, 40 cycles) here, surface energy is considered to be almost fixed. That is, it is expected that it is in the surface concavo-convex structure which is a geometric factor to have caused the super-water repellence of 150° contact angles or more.

In 20 to 30 in which super-water repellence appears cycles, the unevenness has a height of 200-300 nm from AFM 3D image and section analysis. It is thought that air is taken in between concavo-convex with a certain height, and it is thought that the rate of contact between solid liquids decreased sharply, and led to such a dramatic increase in a contact angle by it.

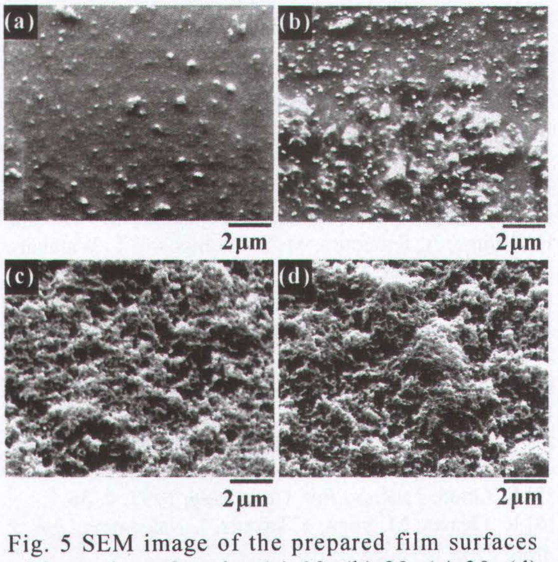


Fig. 5 SEM image of the prepared film surfaces with number of cycles (a) 10, (b) 20, (c) 30, (d) 40.

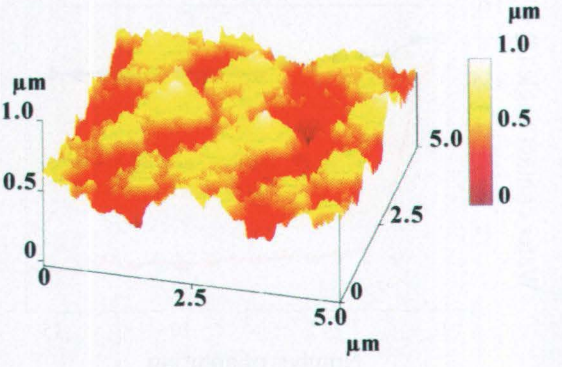


Fig. 6 AFM 3D image of the prepared film surface with the number of 40 cycles.

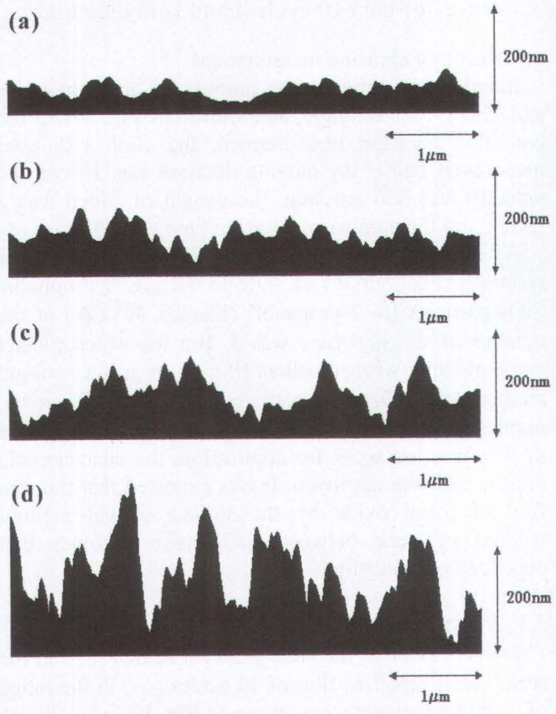


Fig. 7 AFM images of cross sections of the prepared film surfaces with the number of cycles (a) 10, (b) 20, (c) 30, (d) 40.

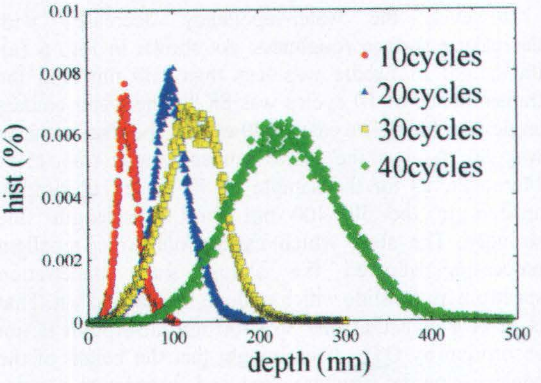


Fig. 8 Bearing analysis of prepared film surfaces with the number of cycles ●10,▲20, ■30,◆40.

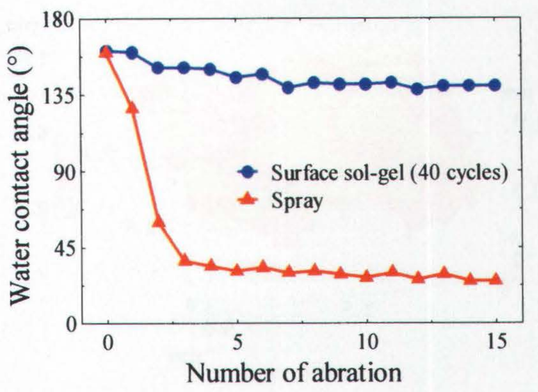


Fig. 9 The relationship between the number of abrasion times and water contact angle of surface sol-gel (40 cycles) and spray method.

3.4. Result of abrasion measurement

Relationship between the number of abrasion times and water contact angle was shown in Fig. 9. As the condition abrasion measurement, the cloth was used non-woven fabric, the moving distance was 10 cm, the velocity was 600 mm/min, the weight of added was 2 g/cm^2, and the number of abrasion time was 15 times.

As shown Fig. 9, the water contact angle of the super water-repellent surface of sprayed 0.2 g/L hydrophobic SiO_2 particles (in 2-propanol) changed 30° (▲) at the number of abrasion time was 5. But the water contact angle of super water-repellent film of the surface sol-gel method and SiO_2 nano particles kept 140° (●) at the number of abrasion time was 15. Although the hardness of film was too weak for application, the characteristic of abrasion was improved. It was expected that the thin film of metal oxide by the surface sol-gel method worked of neck between SiO_2 nano particles that deposited on a substrate.

3.5. Transmittance

Transmittance of the slide glass substrate (—) and the super water-repellent film of 40 cycles (---) in the range of visible wavelength was shown in Fig. 10.

As shown in Fig. 10, the transmittance of the prepared film with 40 cycles was about 70-90%. The surface roughness should be small for transparency, as described above.

However, the water-repellency decreases with decreasing surface roughness. As shown in Fig. 6 (a), the height of needle was less than 100 nm, and the transmittance of 10 cycles was 88 %, the water contact angle was 111°. The case of 40 cycles, the transmittance was 80 %, but the water contact angle was 159°. Moreover, as for the sample of 40 cycles, absorption appears in the 300-400 nm short wavelength side strongly. The slide which carried out water-repellent processing showed the almost same penetration spectrum as the slide which nothing has carried out. That is, it is shown that this 300-400 nm absorption is not absorption by OTS. It is thought that the height of the concavo-convex structure produced in order to acquire the transparency of visible light and to suppress the dispersion phenomenon of light must be made below into 400 nm at least.

To obtained both transparency and water-repellency, the height of needle should be controlled between the range of 200-300 nm.

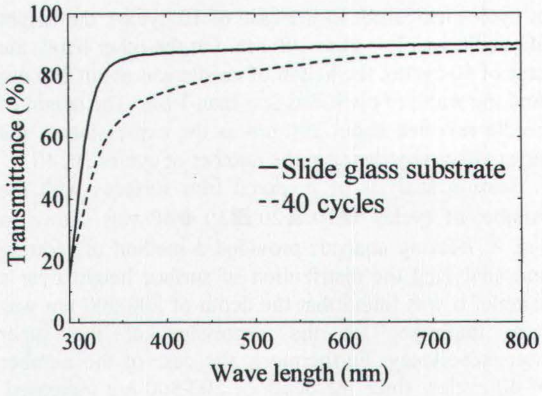


Fig. 10 Transmittance of the prepared film with 40 cycles and slide glass substrate in the visible wavelength.

The roughness of the film obtained from this process depends on the following factors: (1) particle size, (2) the number of cycles by the surface sol-gel method. The size of SiO_2 particles used in this study was 12 nm. Since this particle size was small enough not scatter light, we expected that it was only necessary to control the number of cycles.

4. CONCLUSION

In the present study, the super water-repellent film surface was prepared by the surface sol-gel method and SiO_2 nano particles. The super water-repellent surface showed visible light transparency and hardness of abrasion. Although the preparation of super water-repellent surface has been extensively studied, this report was first one that described about water-repellency, transparency, and hardness of the super water-repellent surface together.

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