Enhancement of Visible Light Absorbance and Hydrophobicity by Sputter-Coating of PTFE onto Fine Protrusions Formed by Sputter-Etching of Steels

Rongguang Wang¹, Keijiro Nakasa², Takashi Kubo³, Akihiro Yamamoto³ and Junya Kaneko¹,²

¹Department of Mechanical Systems Engineering, Faculty of Engineering, Hiroshima Institute of Technology, Hiroshima 731-5193, Japan
²Department of Manufacturing Engineering, Faculty of Engineering, Hiroshima Kokusai Gakuin University, Hiroshima 739-0321, Japan
³Asahi Surface Tec LLC, Higashi-Hiroshima 739-0024, Japan

Argon ion sputter-etching was applied to type 316 stainless steel and AISI M2 (JIS SKH 51) steel, and the sputter-coating of polytetrafluoroethylene (PTFE) film was carried out onto the sputter-etched surface. The sputter-etching of the steels formed fine and dense ridge- or column-shaped protrusions with a diameter of 100 nm to 1 µm on the surface. The protrusions of as-sputter-etched type 316 and M2 steels specimens showed low reflectance of visible light smaller than 8.5% and 4.4% respectively, and the sputter-coating of PTFE film reduced the reflectance further to 5.3% and 2.8% as long as the thickness of the film is thin. In addition, the protrusions of both steels sputter-coated with PTFE films showed superhydrophobicity with a contact angle of a water droplet of more than 165°. The superhydrophobicity of the type 316 specimen was still preserved after an ultrasonic vibration test of 3.6 ks in water.

Keywords: sputter etching, steel, protrusion, polytetrafluoroethylene (PTFE), reflectance, superhydrophobicity

1. Introduction

The interests of many researchers on the special functions of micro- or nano-protrusions on the surface of plant leaf,¹ insect cuticle,² moth³ or butterfly eye⁴ and bird feather,⁵ are now developing to a “biomimetic” or “bioinspired” technology.⁶ Modern nanotechnologies accelerate the transfer of various biological functions to the surface of engineering products. One of the typical examples of the functions is high absorbance of visible light brought about by “moth-eye structure”.³,⁷,⁷–¹⁰ Although all the researches in this field are not necessarily bio-inspired ones, the protrusions have been applied to develop anti-reflective surfaces,⁷,⁷–¹⁰ solar selective heat absorbers,¹¹,¹² an electron emitter,¹³ etc. Another example is superhydrophobicity that is often called “lotus effect”¹⁴–¹⁶. The superhydrophobicity has been also adopted in many industrial products not only to prevent drenching of cloths, paints, concretes but also to prevent surfaces from accumulation of rain, snow,¹⁹ ice,²⁰ contamination and corrosion,²¹ etc. The hydrophobicity is usually evaluated by measuring the contact angle of a droplet on a surface,¹⁴–¹⁶ and the superhydrophobicity, or the contact angle exceeding 150°, is achieved only when fine, tall and dense protrusions or particles are coated with a hydrophobic material, such as silicone or fluorocarbon polymers.

The fine protrusions have been fabricated by using various methods: (1) plasma-etching using a mask prepared by lithography,⁷ putting seed materials on a substrate instead of the mask,¹¹,¹² direct sputter-etching without using masks,¹³ (2) chemical vapor deposition to form carbon nano-tubes,²² (3) using pores of anodic alumina as a template and embedding polymer into the pores,²³ extruding polymer through the pores to form nano-fiber,²³ and plating to form silver nanowires²⁴ and gold nano-rods,²⁵ (4) plating and electrochemical reaction to form nano-structures,²⁶ (5) coating of nano particles,²⁷ and (6) direct replication of leaves.¹⁰,²⁸ However, all the above methods use rather complex processes and are not economical. In some cases, the strength and heat resistance of the protrusions are not sufficient for industrial purposes. On the other hand, the authors²⁹–⁴¹ have already reported that the argon ion sputter-etching of stainless steels, low alloyed steels and tool steels produces fine cone- or column-shaped protrusions on the surface. The obtained protrusions have a diameter or a width of 0.1 to 5 µm and the height/diameter ratio of more than 1.5 depending on the materials used. The protrusions formed by sputter-etching will be widely applicable to various engineering purposes due to their multi-functions as well as their simple and economical fabrication process using only argon gas and commercially supplied metals. The protrusions proved to have excellent mechanical properties³³,³⁵,³⁶ with only small decrease in pitting corrosion resistance.³² They can be used as dies to form fine holes on a polymer film to reduce the light reflection or to facilitate the adhesion of printing ink and a transportation roll for papers and cloths, etc. Large surface area of protrusions can be utilized as catalysts or supports of catalytic species. Sharp tips of the protrusions can be used for a cold emitter, a sensor, and a heat sink of micro-machine.

With respect to the light absorbance, the authors³⁷ have already reported that the fine protrusions with less than 1 µm diameters formed on an AISI M2 tool steel absorb more than 95% of visible light and the absorbance is almost constant independently of wave length as long as the light incident angle is smaller than 60°. On the other hand, the light absorbance of protrusions formed on a type 316 stainless steel is not more than 91% because the sizes of protrusions are a little larger than those of the M2 steel. If a higher light absorbance is achieved in stainless steels, the functions of protrusions will be maintained for long period due to their higher corrosion resistance.

The authors³⁸ have also reported that the thermal vapor-deposition of hydrophobic polyethylene or PFDS film on the
protrusions of AISI M2 tool steel and type 316 stainless steel results in the superhydrophobicity, or a maximum contact angle of 170° for the type 316 steel. The deposited film showed high endurance to ultrasonic vibration in water. However, this deposition process is a little complicated because the sputter-etched specimens taken out of the vacuum chamber should be moved to a furnace for vapor deposition. Furthermore, the deposited film is too thin to be easily damaged by a friction load. Therefore, it is necessary to develop more simple and efficient methods to deposit a relatively thick hydrophobic film with strong cohesion to the protrusions.

In order to solve the above two problems at the same time, the sputter-coating of a hydrophobic PTFE (polytetrafluoroethylene, Teflon®) film with high strength, high thermal and chemical stabilities was carried out on the protrusions just after the sputter-etching by using the same sputter apparatus. If the sputtered PTFE film decreases the spaces among protrusions, it will improve the light absorbance with keeping superhydrophobicity. As is well known, a moth flies at night even in a moist atmosphere because the fine protrusions on moth-eye can absorb very weak light without adhesion of water particles. Also in engineering purposes, there will be some cases that a combination of high light absorbance and superhydrophobicity is necessary. The protrusions formed by the sputter-etching of steels have other special functions of high strength, high electric and thermal conductivities, and high corrosion or oxidation resistance.

2. Experimental Procedures

Commercially supplied type 316 stainless steel with 1 mm thickness and AISI M2 (JIS SKH51) high speed steel with 2 mm thickness were used for the experiments. The chemical compositions of the steels are shown in Table 1. They were cut to square specimens of 20 mm width. All the specimens were polished by emery papers up to #1000, ultrasonically cleaned in acetone, and then set to the stage (type 304 steel disk of 3 mm thick) on the cathode (target side) of an RF magnetron sputtering apparatus (Sanvac Co.: SP300(M)). After the vacuum pressure reached a value lower than 5 × 10⁻⁵ Pa, argon gas (purity: 99.999%) was introduced and maintained at a pressure of 0.67 Pa. The sputter-etching of all the specimens was carried out with a sputter power of 250 W for 0.6–10.8 ks.

After the sputter-etching of the specimens, they were set to the anode of the same sputter apparatus and pre-sputter-etched at 100 W for 300 s to remove a possible oxide film formed on the protrusion surface. Then, the sputtering was carried out using a PTFE (polytetrafluoroethylene; (C₂F₄)ₙ; Teflon®) target at a power of 75 W for 60 s followed by a 600 s rest to cool the target. This cycle was repeated for 1 to 5 times. As a comparison, a thermal vapor-deposition of PFDS (1H,1H,2H,2H-Perfluorodecytriethoxysilane; C₁₆H₁₉F₁₇O₃Si) was carried out by putting the sputter-etched specimens and PFDS liquid separately into a glass beaker, which was sealed with an aluminum foil and kept at 423 K for 1.8 ks in an isothermal furnace.

The surface morphologies of the specimens after the sputter-etching and PTFE- or PFDS-coating were observed by a scanning electron microscope (SEM; Hitachi Co.: S3000H). The surface composition was analyzed by an X-ray photoelectron spectroscopy (XPS; Shimadzu Co.: AXIS ULTRA) using a magnesium target at 15 kV and 10 mA. The analysis was carried out on the region of 2 mm × 1 mm at a vacuum pressure lower than 5 × 10⁻⁷ Pa. The binding energies for function groups in C 1s spectrum are shown in Table 2.

The reflectance of visible light with the wavelength ranging from 400 to 700 nm was measured by a spectrophotometer (Nippon Denshoku Co., LTD., NF333). The reflectance was calibrated by using two standard samples with a reflectance of 87.8% (white standard) and 0% (black). This apparatus is a simple system using light incident angle of 2° and detection angle of 45°, and the measured reflectance is a little larger than the absolute reflectance, e.g. the reflectance of the M2 steel specimen with protrusions measured by this apparatus is 3.8% while the absolute reflectance measured using a gennedoid ellipsoid mirror is 0.25%. The hydrophobicity of the specimen surface was examined by an artificial wetting system equipped with a digital microscope (3R Systems Co.; VT-101). A droplet of pure water with a volume of about 10 µL was put onto the specimen surface using a pipette with a hole of 0.2 mm diameter. The contact angle of the water droplet was determined by fitting the outline of the recorded droplet image to a circle near the intersection of the droplet-air-specimen phases and then drawing a tangential line at that point, with an error of plus or minus 2 degrees. The endurance of the film coated on the protrusions was evaluated from the change of contact angle after an ultrasonic vibration test in pure water using an ultrasonic unit (Branson 2510J-MTH, 42 kHz).

3. Results and Discussion

3.1 SEM observation of protrusions before and after PTFE coating

The type 316 and AISI M2 steels were sputter-etched at a power of 250 W for 0.6–10.8 ks. Figure 1 shows the SEM images of type 316 steel sputter-etched for 0.6 ks (a, a'),

<table>
<thead>
<tr>
<th>Mark</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>W</th>
<th>Mo</th>
<th>Cu</th>
<th>V</th>
<th>Fe</th>
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<tbody>
<tr>
<td>Type 316</td>
<td>0.05</td>
<td>0.40</td>
<td>0.82</td>
<td>0.027</td>
<td>0.001</td>
<td>10.24</td>
<td>17.33</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>AISI: M2(JIS: SKH51)</td>
<td>0.90</td>
<td>0.26</td>
<td>0.30</td>
<td>0.021</td>
<td>0.005</td>
<td>—</td>
<td>4.10</td>
<td>6.15</td>
<td>4.90</td>
<td>—</td>
<td>1.91</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Table 2 XPS binding energies for function groups in C 1s spectrum.

<table>
<thead>
<tr>
<th>Function group</th>
<th>C-C</th>
<th>C-O</th>
<th>C=O</th>
<th>C-F</th>
<th>CF₂</th>
<th>CF₃</th>
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<tbody>
<tr>
<td>Binding energy (eV)</td>
<td>285.0</td>
<td>286.6</td>
<td>288.6</td>
<td>287.5</td>
<td>289.4</td>
<td>291.8</td>
</tr>
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</table>
1.8 ks (b') and 3.6 ks (c) observed at low and high magnifications. When the sputter-etching time is 0.6 ks, larger protrusions are formed preferentially along grain boundaries whereas smaller protrusions are formed in grains, i.e., the size and distribution of the protrusions are inhomogeneous. When the sputter-etching time is increased to 1.8 ks, the protrusions in grains grow to almost the same sizes as those along grain boundaries. The protrusions are ridge-shaped and they are consisted of lines of fine column- or cone-shaped protrusions. The diameter of the protrusions is not the same and a maximum size is smaller than 1 µm. The heights of protrusions are also not the same and the aspect ratio of height to diameter is greater than 3. When the sputter-etching time is 3.6 ks, only a small difference in the sizes remains between the protrusions formed along grain boundaries and in grains. In the case of M2 steel, the size difference among protrusions formed along grain boundaries and in grains disappears at least at a sputter-etching time of 3.6 ks. Although there exist some differences in shape, size, height and distribution among protrusions or between grains and grain boundaries, the area of inhomogeneity is much smaller than those of the reflectance measuring area (8 mm diameter) and the contact area of a water droplet on protrusions (e.g. 1.5 mm, see Fig. 9 shown later). In addition, the reflectance is almost constant independently of the sputter-etching time exceeding 3.6 ks (see Fig. 5 shown later). This means that the sputter-etching time of 3.6 ks is sufficient to obtain stable values of light reflectance and contact angle.

After the sputter-etching of both steel specimens for 3.6 ks, the sputter-coating of PTFE was carried out at 75 W for 60 s (1 cycle) to 300 s (5 cycles). Figure 2 shows the surface morphologies of the type 316 steel just after the sputter-etching (a, a'), and those after the sputter-coating with PTFE for 180 s (b, b') and 300 s (c, c'). The difference in the sizes between the protrusions before and after the 60 s PTFE sputter-coating was not obvious from SEM images. However, when the coating time is 180 s (b, b'), the increase in the diameter of protrusions is visible and there remain fairly wide spaces among the protrusions. According to 180 s sputter-coating of PTFE film on a flat glass plate, the film thickness was about 65 nm. This means that the sputter-coated film corresponding to 65 nm thickness resulted in the distinct change in the SEM images from Fig. 2 (a, a') to (b, b'). When the coating time is 300 s (c, c'), the increase in the diameter of protrusions or the decrease in the spaces among them as well as the blunting of the tip of protrusions is obvious. The SEM image of PFDS vapor-deposited protrusions is omitted here, but the images are not so different from those of as-sputter-etched specimens.

Figure 3 shows the surface morphologies of AISI M2 steel just after the sputter-etching (a, a'), and those sputter-coated with PTFE at 75 W for 180 s (b, b') and 300 s (c, c'). Ring-shaped protrusions with maximum size of about 3 µm exist on the top views (a–c), but the 45° inclined side views (a'–c') indicate that they are consisted of fine wall- or column-shaped protrusions. The thickness of each wall is smaller than 0.5 µm, which is a little smaller than the column diameter of type 316 steel. As shown in Figs. 3 (b) and (c), similar to type 316 steel, the sputter-coating of PTFE after sputter-etching decreases the sharpness of protrusion and the spaces among protrusions.

Although there are some differences in the shape and size of the protrusions in the two steels, the individual protrusion is very fine. A detailed explanation on the formation, growth and decay processes of the protrusions with increasing sputter-etching time is omitted in the present paper, but the fine ridge- and ring-shaped protrusions observed in
Figs. 1, 2 and 3 are considered to be formed in the decay process of conical protrusions.

3.2 XPS analysis of PTFE film on protrusions

Figure 4 shows the XPS C 1s spectra of the specimens after sputter-etching (a), sputter-etching and PFDS vapor-deposition (b), sputter-etching and PTFE sputter-coating (c) as well as that of a PTFE plate used as the sputter target (d). Three function groups of C-C, C-O and C=O are detected on the as-sputter-etched surface (a), which are almost the same function groups from the adsorption of organic contaminants in air as those often appear on a flat metal surface.38,42) On the PFDS vapor-deposited specimen (b), the function groups of CF$_2$ and CF$_3$ are detected in addition to the C-C and C-O peaks observed for the as-sputter-etched surface (a). The former two function groups come from the PFDS molecules, which prove the physical adhesion of PFDS on the protrusions without decomposition. The high content of C-C binding peak corresponds both to the peaks from PFDS and air contaminants.
The C-C peak that appears on the sample (a) is not detected on the PTFE plate, perhaps because the C-C function peak on the sputter-coated surface is caused by the weakening of CF₂ bindings and not from air contaminants. The analyses indicate that the decomposition of PTFE molecules occurs after the sputter of PTFE target and results in the formation of a complex fluorocarbon film containing four types of function groups on the protrusions. This corresponds that the type 316 steel have many wide spaces among protrusions that are different from that of PTFE itself, the surface of M2 steel is black to the naked eye while that of the type 316 steel is dark gray. This corresponds that the type 316 steel have many wide spaces among protrusions that are longer than the wave length of visible light and partly reflect the incident light.

On the other hand, four peaks of CF, CF₂, CF₃ and C-C are detected on the PTFE sputter-coated surface (c), whereas the PTFE plate (d) reveals only the CF₂ peak except an unknown peak marked as ▲. The C-C peak that appears on the sample (a)–(c) is not detected on the PTFE plate, perhaps because the peak form CF₂ (F-C-F species) is much stronger than that from C-C bonding in PTFE and in contaminants. It is possible that the C-C function peak on the film(e) is caused by the weakening of CF₂ bindings and not from air contaminants. These analyses indicate that the decomposition of PTFE molecules occurs after the sputter of PTFE target and results in the formation of a complex fluorocarbon film containing four types of function groups on the protrusions. Although the structure of the sputter-coated film is different from that of PTFE itself, the film is called “PTFE film” in this work for the convenience. In fact, the film sputter-coated on a flat glass plate has revealed almost the same contact angle (120°) with the PTFE plate.

3.3 Reflectance of visible lights

First, the visible right reflectance was measured on the type 316 and M2 steels sputter-etched at 250 W for 0.6–10.8 ks without PTFE sputter-coating. The light reflectance of each specimen was almost constant independently of wave length from 400 nm to 700 nm except for the type 316 steel specimens sputter-etched for 0.6–1.8 ks where a small decrease in the reflectance occurred at a longer wave length. Figure 5 shows the relationships between sputter-etching time and average value of visible light reflectance from 400 nm to 700 nm obtained for both steels. The reflectance is smaller for M2 steel than that of type 316 steel when the sputter etching time is longer than 1.8 ks and they are almost constant independently of sputter-etching time. The exact comparison of protrusion densities between two steels is difficult from the images in Figs. 2(a, a’) and 3(a, a’), but the surface of M2 steel is black to the naked eye while that of the type 316 steel is dark gray. This corresponds that the type 316 steel have many wide spaces among protrusions that are longer than the wave length of visible light and partly reflect the incident light.

Figures 6 and 7 show the relationships between wave length and reflectance of visible light obtained for the protrusions of type 316 and M2 steels that were PTFE sputter-coated after sputter-etching for 3.6 ks. Although the reflectance varies depending not only on the wave length but also on the sputter-coating time, the following common but a little different tendencies exist in both steels. Firstly, the reflectance of as-sputter-etched steels is almost constant independently of wave length as described above, which means that the protrusions with random sizes at least from 400 nm to 700 nm are homogeneously distributed. The average reflectance of the type 316 and M2 steels are 8.5% and 4.4% respectively. Secondly, the following dependences of reflectance on wavelength and sputter-time are observed for both steels: (1) The increase in the sputter-coating time until 120 s reduces the reflectance to 5.3% for the type 316 steel and to 2.8% for the M2 steel, and the reflectance is not so largely dependent on wave length. (2) When the sputter-coating time exceeds 180 s, the reflectance in the short wave length region increases largely. (3) When the coating time is 300 s, the reflectance in the short wave length region decreases again. Thus, the effect of PTFE coating time on the reflectance is complex especially when the coating time is longer than 180 s.

As is well known, the mechanism of visible light absorbance due to fine protrusions or the “moth-eye
structure”, is the restrictions of an incident light into the spaces among protrusions due to the repeated reflections of the light on the protrusion surfaces when the protrusion size is comparable to the wave length of the incident light. If the protrusions are coated with a film, the thickness, transparency, and refractive index of the film also affect the total reflectance. The PTFE plate used as a sputter target is not transparent but of milky white color. Figure 8 shows the wave length dependency of absorbance (not reflection) of the flat PTFE plate of 5 mm thickness. The absorbance gradually increases form 5% to 25% with increasing wave length.

The above complex light reflection behaviors due to PTFE sputter-coating, (1)–(3), can be qualitatively explained by the light reflection mechanism and the characteristics of PTFE film as follows: When the sputter-coating time is shorter than 120 s, the film is very thin and the shapes and sizes of the protrusions will not be actually changed, though the PTFE coating shrinks the spaces among protrusions more or less. On the other hand, the PTFE film on the protrusions refraacts the incident light (refractive index of PTFE is more than 1.3) and introduces the reflected light deeper to the bottom of the protrusion. The PTFE film itself absorbs the incident light though the absorbance of the film is not so large (Fig. 8). These effects explain the result (1), i.e. the decrease in the reflectance with a small wave length dependency. When the coating time is 180 and 240 s, the sputtered PTFE film increases the diameter of protrusions and fills the spaces between protrusions. If the depth of the spaces decreases, then the reflectance increases. However, there are many protrusions with larger diameters more than 700 nm (Figs. 2(b) and 3(b)). So that, even if small spaces among small protrusions are filled by the PTFE film, the reflectance in the longer wave length will not be so increased. On the other hand, the sharpness of protrusions decreases and the absorbance of PTFE film itself is small in the short wave length region (Fig. 8). These effects explain the result (2), or the increase in the reflectance especially in the short wave length region. With further increase in the coating time to 300 s, the diameter of protrusions increases and the direct reflection from the top of the protrusions increases the average reflectance. However, the numbers of narrow spaces are rather increased by the filling of PTFE as is shown in Figs. 2 (c) and 3(c), and this again lowers the reflectance in the shorter wave length region. This explains the result (3).

Although the reflectance depends on the coating time or the film thickness complexly, it is understood that the coating of PTFE is effective to lower the reflectance as long as an optimum coating time (e.g. 120 s) or film thickness (e.g. smaller than 65 nm) is selected.

3.4 Superhydrophobicity of protrusions sputter-coated with PTFE

Figure 9 shows the effect of PTFE sputter-coating or PFDS vapor-deposition time on the contact angle of a water droplet on the sputter-etched type 316 steel specimens. The contact angle increases to a superhydrophobic value of 168° after the PTFE sputter coating of 60 s, and the angle does not largely vary with increasing sputter-coating time. A maximum contact angle is 174°, and the water droplet easily rolls away from the surface even by a small tilting of the sample, i.e. the advancing and receding angles are almost the same, and the hysteresis is very small. Also for the type 316 steel vapor-deposited with PFDS at 423 K for 1.8 ks, the contact angle of 165° was obtained, which is almost the same value as that reported in the previous paper. The contact angles of M2 steel sputter-coated with PTFE for 60 to 300 s were almost 165°. This is a little smaller than that of the type 316 steel, but it is sufficiently within the superhydrophobic range.

From the above results, it is understood that the superhydrophobicity is obtained also by the sputter-coating of
PTFE and this process is more simple and efficient than the PFDS vapor-deposition. As has been already explained in the previous paper, the superhydrophobic behavior of a droplet on the protrusions is expressed by Cassie and Baxter equation:44)

\[
\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2
\]

Where, the subscripts 1 and 2 express composition 1 (the sputter-coated PTFE film) and composition 2 (air), \( \theta_1 \) and \( \theta_2 \) are contact angles of a water droplet on a flat surface of each composition, \( f_1 \) and \( f_2 \) are relative contact area-ratios of each composition supporting a droplet \( (f_1 + f_2 = 1) \), \( \theta' \) is the contact angle of a water droplet on the surface with protrusions. Because the contact angle of a water droplet on air, \( \theta_2 \), is 180°, and by using the measurements that the contact angle of a water droplet, \( \theta_1 \), on the sputter-coated PTFE film on a flat glass is 120°, and the contact angle of a water droplet, \( \theta' \), on the 180 s PTFE-coated protrusions of type 316 steel is 170° (Fig. 9), the calculated contact area ratio \( f_1 \) of a droplet is 3.0%. This means that the water droplet is supported mainly by the air among protrusions. The similar value of 3.5% is calculated for the protrusion of type 316 steel vapor-deposited with PFDS for 1.8 ks.

In the previous paper, the authors reported the contact angles of a droplet on different types of protrusions of cone- and ring-shapes, and found that the contact angle is not so dependent on the protrusion shape as long as they are fine enough and have multi-scaled protrusions with random size, height and distribution. According to the SEM images shown in Figs. 2 and 3, the spaces between protrusions become narrow by the sputter-coating of PTFE, but the contact angle is not so changed as is shown in Fig. 9. Thus, the superhydrophobicity or contact angle seems to be no longer dependent on the shape of protrusions when the superhydrophobicity approach a maximum limit both by the appropriate combinations of the multi-scaled protrusions and the coating of hydrophobic film.

### 3.5 Evaluation of endurance of sputter-coated film on the protrusions by ultrasonic vibration test

The endurance to wear and delamination of the superhydrophobic film on the protrusions is one of the most important factors especially when the surface of products receives a contact or friction force. In order to simply evaluate the endurance of the films, an ultrasonic vibration test was carried out in water where the damage and delamination of film can occur due to repeated cavitation attack and vibration of slender protrusions.

Figure 10 shows the effect of ultrasonic vibration time on the contact angles of a water droplet measured on the type 316 and M2 steels PTFE sputter-coated for 180 s as well as the type 316 steel PFDS vapor-deposited for 1.8 ks. Each value is average obtained from the tests on 6 different positions of each specimen, and the measurement is repeated almost on the same position on the same specimen after every vibration tests. According to this figure, the contact angle of the type 316 specimen decreases a little but the decrease is smaller for the PTFE sputter-coating than that of PFDS vapor-deposition, and the superhydrophobic angle of 150° is maintained for the PTFE sputter-coated type 316 steel even after the 3.6 ks vibration time. The decrease in the contact angle is attributed to the partial delamination of films on the top of the protrusions. A difference in the decrease in the contact angles of both films can be explained by a difference in the cohesion mechanism, i.e. the PFDS vapor-deposition is a physical adhesion prevented by the pre-adhered air contaminants on the protrusions, whereas the sputter-coating of PTFE was carried out on a fresh surface after the pre-sputter-etching of protrusions and the PTFE molecules adhere with much higher speed than PFDS molecules although the PTFE structure has decomposed to short chains with CF, CF₂, CF₃ and C-C functions.

On the other hand, the hydrophobicity of the PTFE-coated M2 steel is quickly lost and the contact angle decreases to 80° after the ultrasonic vibration test of only 300 s. The cavitation attack must have resulted in a partial delamination of PTFE film on the top of the protrusions of M2 steel within a short time, though no obvious change in the SEM images was found after the ultrasonic vibration test of 3.6 ks. Because the corrosion of protrusions along the interface is not so large within 300 s, the reason why such a large difference in the endurance appears in the vibration test is not clear even if the interfacial strength of M2 steel is smaller than that of the type 316 steel just after the sputter-coating of PTFE.
As is described above, the coating of PTFE film increases both the absorbance of visible light and the hydrophobicity at the same time. In the present paper, only one usage of such a surface with low reflectance and superhydrophobicity is introduced. Consider the case that a dark or black plate with fine protrusions is used as a back plate of a signal or an illumination outdoor. The back plate absorbs not only the sunshine but also the light from other sources, and one can distinguish the signal clearly from other lights even in the evening when many light sources are mixed. Rain and fog do not adhere on the plate and the contaminants on the surface are removed with rain drop. In this case, main function is low reflectance and others are superhydrophobicity and corrosion resistance of the protrusions.

4. Conclusions

Argon ion sputter-etching was applied to type 316 and AISI M2 (JIS SKH 51) steels to form fine protrusions. Sputter coating of PTFE (polytetrafluoroethylene) and thermal vapor-deposition of PFDS (1H, 1H, 2H, 2H-Sputter coating of PTFE (polytetrafluoroethylene)) and Perfluorodecyltriethoxysilane) was carried out onto the protrusions after the sputter-etching. The reflectance of visible light and the hydrophobicity were measured. The results obtained are as follows.

1. The sputter-etching of both steels formed column- or wall-shaped fine protrusions with a diameter or thickness of smaller than 1 µm on the surface.

2. Reflectance of visible light decreased with increasing sputter-coating time of PTFE as long as it is shorter than 120 s. The smallest reflectance of the protrusion obtained by the sputter-coating of PTFE was 5.3% for the type 316 steel and 2.8% for the M2 steel.

3. Superhydrophobicity with a contact angle of a water droplet of more than 165° was obtained both by the sputter-coating of PTFE film on the sputter-etched type 316 and M2 steels and the vapor-deposition of PFDS film on the type 316 steel. The contact angle of PTFE film is not so varied with increasing sputter-coating time within 300 s. The endurance of the sputter-coated PTFE film on the type 316 steel evaluated by the ultrasonic vibration test in water was higher than that of thermally vapor-deposited PFDS film.

4. The sputter-coating of PTFE film after sputter-etching is a simple and effective method to improve light reflectance and hydrophobicity of protrusions at the same time.

REFERENCES