Adhesion of Atmospheric Micro-Contaminants on SUS304 Steel and Removal by UV Illumination*1

Rongguang Wang*2, Mitsuo Kido, Suketsuku Nakanishi and Takuji Okabe

Department of Mechanical Systems Engineering, Faculty of Engineering, Hiroshima Institute of Technology, Hiroshima 731-5193, Japan

Micro-contaminants on SUS304 stainless steel were observed and confirmed by atomic force microscope, and the micro-contaminant removal was carried out by ultraviolet (UV) illumination. With an increase in the holding time in air, particle- and film-like micro-contaminants appeared and their amount increased on the specimen surface. Then, the amount of particle-like contaminants decreased and finally almost all the surface was covered by film-like contaminants. The amount of micro-contaminants on the specimen surface decreased with an increase in the UV illumination time, with extensive removal of the organic substance in the contaminants but leaving part of the contained water in the contaminants. The micro-contaminants slowly re-adhered on the treated surface when the surface was re-exposed to air, with a longer period than 172 ks for the recovery to the state before the UV illumination. The surface for macro-droplets after the UV illumination became hydrophilic, while no large change of the wettability for micro-droplets on the same surface can be observed.

1. Introduction

Surface cleaning is commonly a necessary process in many industry fields. For example, an ultraclean surface is important before and after a surface modification in the case of getting suitable surface properties of adhesivity, conductivity, wearability, corrosion resistance and photocatalysis ability.1–7) It is known that most of the contaminants can be successfully removed by various methods, however, the removal of micro-contaminants (air contaminants containing organic contaminants and water) is still a difficult work.8,9) Before removing them as much as possible, it is necessary firstly to know the adhesion behavior of such micro-contaminants on the solid surface.

Many researches had been reported on cleaning contaminants from solid surfaces.2–8) However, the removal of micro-contaminants basing on direct observation has not been investigated, due to the difficulty in observation small, soft and evaporable micro-contaminants. In most reports, the cleanliness of a surface was generally checked by analyzing the utmost surface composition in vacuum or measuring the wettability of a millimeter-scale water droplet in air. No reports can be found on the estimation of the amount of micro-contaminants by the in-situ observation. Previously, the authors observed and confirmed micrometer-scale contaminants on metallic surfaces with an atomic force microscope (AFM) in the AC noncontact mode (AC-mode) and the contact mode (C-mode).9–11) The atmospheric micro-contaminants containing both of organic species and water were considered to be not uniformly distributed on the surface. This seems to be one of the reasons that the contact angle of a micrometer-scale droplet (micro-droplet) of water is much smaller than that of a millimeter-scale droplet (macro-droplet) of water on the surface.11,12) However, the adhesion behavior of the micro-contaminants on the metallic surface when increasing the exposure time in air has not been known and, of course, the removal of the contaminants by a certain cleaning process has not been investigated.

It is known that the ultraviolet (UV) light can be used to clean solid surfaces.2–4) However, as mentioned above, the direct confirmation of the removal of micro-contaminants by UV light illumination has not been checked yet. In this work, the adhesion behavior of micro-contaminants on SUS304 stainless steel with the increase in the air exposure time was investigated and the surface was illuminated by UV light in order to remove the contaminants for obtaining an ultraclean metallic surface. The reason for using the stainless steel is that, there is a compact passive film on the surface thus the adhesion of water only brings about slight oxidation of the surface even for a long time. The surface after illumination was checked by direct observation by AFM,9–13) wetting measurement with macro- and micro-droplet of water,11) and XPS analysis.

2. Experimental Details

Commercially supplied JIS SUS304 stainless steel sheet (thickness: 2 mm; Composition: C:0.05 mass%, Si:0.63, P:0.032, S:0.002, Ni:8.10, Cr:18.05, Fe: Bal.) was used for preparing specimens. All specimens were wet-polished with alumina powder (mean diameter: 0.05 μm) and ultrasonically cleaned in acetone for 2.7 ks (3 times × 0.9 ks; with changing the acetone in each time). After then, the specimen surface was observed by atomic force microscope (AFM; Shimadzu Co., SPM-9800) in air (293 ± 3 K; 50~60%RH). After the specimens were kept in a dessicator (air, 293 ± 3 K, and 25~30%RH) for a prescribed exposure period, the surfaces were 0.6, 1.2 ks or 3.6 ks illuminated with UV light in air (293 ± 3 K; 50~60%RH). After the specimens were kept in a dessicator (air, 293 ± 3 K, and 25~30%RH) for a prescribed exposure period, the surfaces were 0.6, 1.2 ks or 3.6 ks illuminated with UV light in a sealed chamber (Iwasaki Electric Co., Ltd., OC-256015), and then observed again by AFM. Figure 1 shows the schematic drawing of the apparatus with six quartz lamps (Iwasaki Electric Co., Ltd., QOL 25SY; 25 W × 6), which
emit UV light with main wavelengths of 185 nm and 254 nm. During the illumination, part of oxygen (O$_2$) sealed in the chamber will be changed to ozone (O$_3$), and the sealed air was vented after the illumination.

The specimen surfaces before and after the air exposure in dessicator or after the UV light illumination were immediately observed by AFM in the AC-mode and the C-mode in air (293 ± 3 K and 50–60%RH). In the C-mode observation, only the hard substrate of the specimen can be observed because the tip of the cantilever strongly touch the surface and soft contaminants will be displaced out of the observation area, whereas in the AC-mode, the morphology of the adhered soft contaminants can be observed because the force between the tip and the contaminants is much smaller than that in the C-mode.\textsuperscript{11,12} In detail, a wide area was observed in the AC-mode and then the central narrow area among the wide area was again observed in the C-mode. By this way, the estimation of the amount of adhered contaminants on the surface was tried.

The surface compositions before and after the UV illumination were analyzed by X-ray photoelectron spectroscopy (XPS; Shimadzu Co., AXIS ULTRA; vacuum: <5 × 10^{-7} Pa). In addition, the wettability of the millimeter-scale macro-droplet and the nanometer-scale micro-droplet of water on the specimens was measured by the digital microscope or the AC-mode of AFM.

3. Results and Discussion

3.1 Observation of micro-contaminants

Figure 2 shows the specimen surfaces after the polishing and ultrasonic cleaning in acetone. The surfaces were respectively observed by the C-mode and the AC-mode of AFM. In all the AFM images in this paper, the higher brightness means the larger height there; the maximum height in the right histogram was adjusted to show a clear surface in the observed region. In Fig. 2(a), nothing can be found except polish scratches in the C-mode AFM image. Fig. 2(b) shows the same surface with Fig. 2(a) but it is observed in both the AC-mode and the C-mode. The surface observed in Fig. 2(b) is different from that in Fig. 2(a), particle- and film-like things appeared on the surface. These are considered to be the micro-contaminants adsorbed from the air. Moreover, the contaminants are soft because they can be swept out from the C-mode scanned area (b2) by the AFM probe (b3). Such micro-contaminants should be the same things with that obtained in the previous report, i.e., containing organic contaminants and water.\textsuperscript{10,11}

Figure 3 shows the specimen surfaces after different exposure time to air. After the 350 ks exposure (a1), particle- and film-like contaminants were observed on the surface, almost the same with that observed in Fig. 2(b). The swept-out contaminants by the C-mode scanning (Fig. 3(a2)) was seen in the Fig. 3(a3). The amount of contaminants after the 600 ks exposure seemed to be more than that after the 350 ks exposure (Fig. 3(b1), (b2), (b3)). The particle-like contaminants increased both in size and in number. On the other hand, the increase of the contaminants cannot be seen after 1200 ks exposure (c1), but more film-like contaminants were observed within the narrow observation region (500 nm × 500 nm). The film-like ones almost covered the entire surface. Such film-like contaminants were also found on the long time exposed pure iron and pure zinc surfaces.\textsuperscript{13} This means the adsorbed micro-contaminants had become stable film-like ones after a long period exposure in the air.

3.2 Removal of contaminants by UV illumination

Figure 4 shows the specimen surfaces after 600 ks air exposure and then UV light illumination for 0.6 and 1.2 ks. The polish scratches, which had been almost covered by micro-contaminants before the UV illumination (Fig. 3(b)), clearly appeared on the surface in the AC-mode observation after the 0.6 ks illumination. In addition, the particle-like contaminants disappeared while the film-like ones kept being stayed on the surface (Fig. 4(a2), (a3)). This means that most of the contaminants have been removed by the UV illumination and leaving only a small amount of them on
the surface (a3). Figure 4((b1), (b2), (b3)) shows the surface after the 1.2 ks illumination. The contaminants further decreased with the increase in the UV light treatment time. However, the thin film-like contaminants still covered the surface. On the 3.6 ks illuminated surface, almost the same result was obtained with that after 1.2 ks. The contaminants can not be thoroughly removed.

Figure 5 shows the calculated mean thickness of contaminants on surfaces after different surface treatments (i) before UV-O3 treatment (UV(0 s)), then (ii) after 0.6 ks UV treatment (UV(0.6 ks)), (iii) after 1.2 ks UV treatment (UV(1.2 ks)) or (iv) after 3.6 ks UV treatment (UV(3.6 ks)). The amount of micro-contaminants was obtained by a trial calculation of the three-dimensional volume of a region A (e.g., 2μm × 2μm) from the lowest base point in the C-mode scanned area B (e.g., 500 nm × 500 nm). The volume was divided by the total area (e.g., 4 μm²) to get the mean thickness of micro-contaminants. More than three observations for each type of condition were carried out. As the result, the mean thickness of contaminants on the 600 ks exposed surface was about 18 nm, whereas it became about 12 nm after the 0.6 ks illumination, about 6 nm after the 1.2 ks illumination and about 3 nm after 3.6 ks illumination. According to this, it is known that the micro-contaminants can be removed by the increase in the illumination time. However, such thickness values can only be used as reference data because (1) the surface roughness was neglected in the calculation and (2) not all the contaminants can be swept out of the C-mode scanning region. The amount of contaminants on the UV-illuminated surface should be much smaller.

Figure 6 shows the 1.2 ks UV-illuminated surfaces after further re-exposure to air for 350, 600 and 1200 ks. The re-adhesion of contaminants on the surface occurred, but the amount seemed smaller than that without UV light illumination (Fig. 3). The slight re-adsorption of micro-contaminants might be attributed to the decrease in the amount of base OH groups (M-OH2+) on the metallic surface, which promote the adhesion of the COOH group in the organic contaminants.14,15) The re-adhered contaminants were mainly film-like ones.

### 3.3 Surface composition analysis by XPS

Figure 7 shows the relative atomic concentration of surface elements obtained from the XPS analysis. The specimens are respectively treated after (i) 700 ks exposure...
in air (UV(0 s)), (ii) 1.2 ks ultrasonic cleaning (US(1.2 ks), (iii) 1.2 ks UV illumination (UV(1.2 ks)), or (iv) 0.3 ks Ar⁺ etching (Ar⁺(0.3 ks)). The element of carbon is the main component of organic contaminants, which slightly decreased after the ultrasonic cleaning, but markedly decreased after the UV illumination becoming very close to that value after the Ar⁺ etching. In addition, the metal elements of Fe largely increased after the UV illumination. This means that the removal effect of contaminants by UV illumination is remarkable. On the other hand, oxygen increased in spite of the existence of the C-O and C=O groups in the organic contaminants. This would relate to the oxidization of the surface with active oxygen atoms and ozone molecules. Such oxidants can be produced in the illumination under the sealed condition.4,5)

This result corresponds well with the AFM observation. However, the AFM observation was carried out in air and the XPS analysis was performed in a vacuum lower than 5 × 10⁻⁷ Pa. Some water was evaporated and mainly the organic contaminants were detected by XPS. This can be used to explain the difference between the calculated large thickness of contaminants on the 600 ks-exposed surface (about 18 nm) from the AFM image in air and the appearance of strong peaks of metals in the XPS analysis. In general, only a thin surface layer with several nanometers thickness on the specimen can be detected in the XPS analysis. This contrasting result is also due to other two factors: one is that the surface was not entirely covered by the contaminants, and the other is that the mean thickness of the layer of contaminants was over-calculated because the surface roughness of the specimen was neglected in the calculation.

### 3.4 Wettability measurement

Corresponding to the specimens in Fig. 2 and Fig. 3, a macro-droplet of water with millimeter-scale was put on the specimens after acetone cleaning (i) and further exposure in air (ii). The contact angles were obtained as 53° (air exposure: 0 ks), 51° (350 ks), 40° (600 ks) and 41° (1200 ks), respectively. Accordingly, the surface became a little hydrophilic with the increase in the air exposure. This means that the organic contaminants cannot continually increase on the surface; the amount change of the contaminants are mainly due to the adsorption and the evaporation of water in air during the air exposure.
Figure 8(a) shows the millimeter-scale macro contact angles on specimen surfaces corresponding to those treated specimens in Fig. 7. The errors bars were not shown in the figure because they are very small. The contact angle clearly decreased with the increase in the UV illumination time, particularly the angle after 3.6 ks is only $1/4$ of that before the UV illumination. This is due to the removal of hydrophobic organic contaminants on the surface. In the previous report, the air contaminants were proposed to be composed from two layers: the out layer is hydrophobic organic contaminants.
organic contaminants and inner layer is water. The wettability is mainly determined by the utmost outer surface; accordingly it is clear that the out organic contaminants had been removed by UV illumination. On the other hand, Fig. 8(b) shows the micro contact angles of nanometer-scaled water droplet on the 350 ks exposed surface before and after 3.6 ks UV illumination. The error bars (standard deviation) are shown in the figure. The horizontal radius of the micro-droplet of water used for getting the contact angle is about 65 nm. On the not illuminated surface, the contact angle for micro-droplet is much smaller than that for the macro-droplet, which corresponds well to the previous reports. However, no difference on contact angles between specimens before and after 3.6 ks UV illumination can be found on the 3.6 ks illuminated surface. This should be attributed to the distribution of organic contaminants on the surface, i.e., the organic contaminants do not cover all the surface and micro-droplet occupies only the positions without organic one. Thus, the contact angle of micro-droplet was not largely influenced by the amount of the organic contaminants. In addition, the macro contact angle on specimens after 1.2 ks or 3.6 ks UV illumination is almost the same with that measured by micro-droplet. This indicates that almost all the organic contaminants had been removed by the UV illumination.

Furthermore, the macro contact angle of water on 1.2 ks UV illuminated specimen was measured after 3.6, 14.4, 86.4 and 172.8 ks air exposure. The values were respectively 19°, 24°, 27° and 40°. It means that the organic contaminants gradually re-adhered on the cleaned surface; but a period longer than 172 ks is necessary to recover back to the surface state before the illumination. Presuming that the contact angle of macro-droplet on bare surface without organic contaminants is 10° (Fig. 8) and that of the fully covered surface is 70°, the surface coverage of organic contaminants can be calculated by the Cassie-Baxter equation. The value is 0% after 1.2 ks UV illumination, and it changed to 6%, 11%, 15% and 34% after 3.6 ks, 14.4 ks, 86.4 ks and 172.8 ks in air.

3.5 Mechanism of removal of micro-contaminants

In this work, two main types of UV light with wavelengths of 185 nm and 254 nm were emitted from the lamps. The 185 nm light with higher energy can break the C-C, C-H and C-O bondings in the organic contaminants and the O-O bonding in air. Some active oxygen atoms from the broken O-O bonding can promote the formation of ozone molecules (O$_3$). The O-O bonding in O$_3$ can also be broken by the 254 nm UV light to form active oxygen atoms. Both the active oxygen atoms and ozone molecules are strong oxidants. They can directly oxidize the organic contaminants and bind to the active C and H atoms from the broken C-C, C-H and C-O bondings. The result is that the organic contaminants decomposed to CO$_2$ and H$_2$O, equal to the removal of the micro-contaminants from the surface. On the other hand, H$_2$O can be adhered onto the surface again. It means that the adsorbed water on the surface is difficult to be removed in this way.

It has been known that most of the organic contaminants can be removed by the UV illumination according to the above XPS analysis and the wettability evaluation. However, according to the AFM observation the contaminants cannot be completely removed even after a long-time illumination. This indicates that the remaining contaminants should be mainly water and the removed contaminants should be mainly the organic species. According to the micro wetting observation, it is known that the adhesion of micro-droplets is not so many. In addition, the re-adhesion will occur on the surface during the period from the finish of the UV illumination to the beginning of the AFM observation. This indicates that the residual contaminants observed by AFM after a long time exposure on the UV illuminated surface will be mainly the water and a little of organic contaminants. Of course, the re-adhered contaminants will be less than that before the illumination. Since the re-adhesion during a short period is still unknown, this should be clarified by observing the surface with simultaneous illumination by UV lights in the future.

4. Conclusions

Micro-contaminants on SUS304 stainless steel were observed and confirmed by atomic force microscope, and micro-contaminant removal was carried out by ultraviolet (UV) illumination. The conclusions are as follows.

(1) With an increase in the holding time in air, particle- and film-like micro-contaminants appeared and their amount increased on the specimen surface. Then, the amount of particle-like contaminants decreased and finally almost all the surface was covered by film-like contaminants.

(2) The amount of micro-contaminants on the specimen surface decreased with an increase in UV illumination time, with extensive removal of the organic substance in the contaminants but leaving part of the contained water in the contaminants. The micro-contaminants slowly re-adhered on the treated surface when the surface was re-exposed to air, with a longer period than 172 ks for the recovery to the state before the UV illumination.

(3) The surface for macro-droplets after the UV illumination became hydrophilic, while no large change of the wettability for micro-droplets on the same surface can be observed.

Acknowledgements

Part of this work was supported by MEXT.HAITEKU, 2004--; and JSPS Grant-in-Aid for scientific research (18560093).

REFERENCES

4) S. Suzuki, S. Ichimura, A. Kurokawa, Y. Ishikawa, M. Isshiki and Y.
5) M. Yaguchi: Senjyou Gijyutsu Seihin Hyakka, (Kogyo Chosakai
355–364.
605.
395.
s753–s758.
14) J. D. Filius, T. Hiemstra and W. H. Van Riemsdijk: J. Colloid Interface
295.