Plasma-based Fluorine Ion Implantation into Dental Materials for Inhibition of Bacterial Adhesion

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The aims of this study were to evaluate the fluorine depth profiles of pure titanium (Ti), stainless steel (SUS), and polymethyl methacrylate (PMMA) modified by plasma-based fluorine ion implantation and the effects of fluorine ion implantation on contact angle, fluoride ion release, and S. mutans adhesion. Fluorine-based gases used were Ar+ F\textsubscript{2} and CF\textsubscript{4}. By means of SIMS, it was found that the peak count of PMMA was the lowest while that of Ti was the highest. Then, up to one minute after Ar sputtering, the presence of fluorine and chromic fluoride could be detected by XPS in the surface and subsurface layer. As for the effects of using CF\textsubscript{4} gas for fluorine ion implantation into SUS substrate, the results were: contact angle was significantly increased; no fluoride ion release was detected; antibacterial activity was significantly increased while initial adhesion was decreased. These findings thus indicated that plasma-based fluorine ion implantation into SUS with CF\textsubscript{4} gas provided surface antibacterial activity which was useful in inhibiting bacterial adhesion.

Key words: Ion implantation, Fluorine, Bacterial adhesion

INTRODUCTION

In a dental clinic, various kinds of appliances — such as space maintainer and space regainer for occlusal guidance, and also as orthodontic appliances and dentures — are used frequently for children and adults. These appliances are susceptible to adhesion by oral bacteria\textsuperscript{[1-6]}, and thus cause dental caries\textsuperscript{[7-8]}, periodontal disease, or inflammation of oral soft tissue\textsuperscript{[9,10]}.

Plasma surface modification, as an economical and effective material processing technique, is gaining popularity in the biomedical field. It is able to change the surface chemical composition of the processed material as well as improve the latter’s properties such as wettability, adhesion, dyeability, refractive index, hardness, chemical inertness, lubricity, and biocompatibility\textsuperscript{[11]}. As such, in recent years, there is an increasing trend to employ plasma-based ion implantation to modify the surface of biomaterials\textsuperscript{[12,13]}. With plasma-based ion implantation, specimens are immersed in high-density plasma and pulse-biased to a high negative potential relative to the chamber wall. Ions generated in the overlying plasma are accelerated across the sheath formed around the sample and implanted into the sample surface. However, in the event of ditch contours and concave corners, it becomes difficult for the sheath to follow the surface contour of the complex shape. Moreover, in the event of non-uniform plasma density distribution around the matrix, it also becomes difficult to achieve uniform ion implantation on the whole surface. Nonetheless, despite the aforementioned drawbacks, this technique features non-mass analysis, no beam-transport optics, and no focusing or scanning of the beam\textsuperscript{[14]}. Therefore, compared to conventional ion implantation, the plasma-based ion implantation facility is smaller, less expensive, and simpler to maintain and operate\textsuperscript{[15-17]}.

To date, some researchers have carried out surface modification by fluorine ion implantation\textsuperscript{[18-20]} and found it to be a useful means in inhibiting bacterial adhesion. In this study, therefore, the surfaces of Ti, SUS, and PMMA were modified by plasma-based fluorine ion implantation to evaluate this technique’s inhibitory effect against oral bacterial adhesion. It should be highlighted that bacterial adhesion to biomaterial surface is an important step during the initial stages of pathogenic infection. Two methods have been identified to inhibit the formation of microbial plaque. The first method is to inhibit the initial adhesion of oral bacteria, while the second method involves surface antibacterial activity to inhibit the colonization of oral bacteria\textsuperscript{[11,22]}

In view of the beneficial effects of fluorine ion implantation, the aims of this study were to evaluate the depth profiles and XPS spectra of fluorine concentration in the surface of dental materials, as well as evaluate the effects of fluorine ion implantation on contact angle, fluoride ion release, and bacterial adhesion.

MATERIALS AND METHODS

 Plasma-based fluorine ion implantation

The principle of plasma-based ion implantation is shown in Fig.1 (modified from Okui et al\textsuperscript{[21]}).
Plates of Ti (TP340C: 99.98 wt% Ti, 0.003 wt% H, 0.09 wt% O, 0.01 wt% N, 0.07 wt% Fe; Kobe Steel Ltd., Kobe, Japan), SUS (SUS316L: 65.67 wt% Fe, 17.00 wt% Cr, 13.00 wt% Ni, 2.40 wt% Mo, 1.40 wt% Mn, 0.03 wt% C, 0.50 wt% Si; Daido Steel Co. Ltd., Nagoya, Japan), and PMMA (ACRYPET VH #001, Mitsubishi Rayon Co. Ltd., Tokyo, Japan) with size of 10×10×1 mm were used. Before ion implantation, Ti and SUS plates were polished to a mirror-like surface and washed in an ultrasonic bath with 98% ethanol. PMMA plates were wiped with alcohol-soaked cotton. Ti, SUS, and PMMA plates were then modified by plasma-based ion implantation appliance at Ion Engineering Research Institute Co., Osaka, Japan. Fluorine gas for plasma-based ion implantation was used. Conditions of plasma-based fluorine ion implantation are shown in Table 1. For controls, non-fluorine-ion-implanted Ti, SUS, and PMMA were used.

### Secondary ion mass spectrometry (SIMS)

The peak count (count per second, CPS) and depth profile until 10 counts (nm) of fluorine in Ti, SUS, and PMMA samples were measured with a secondary ion mass spectrometer (SIMS) (ADEPT 1010, ULVAC Inc., Kanagawa, Japan). Measurements were carried out using 3.0 keV Cs⁺. For each material, a total of eight samples were prepared for fluorine ion implantation by Ar+F2 gas (i.e., N=4) and CF4 gas (i.e., N=4).

![Fig. 1 Principle of plasma-based ion implantation (modified from Okui et al.23).](image)

**Table 1 Conditions of fluorine ion implantation into surface of dental materials**

<table>
<thead>
<tr>
<th>Gas</th>
<th>Ar+F2 (95% argon and 5% fluorine)</th>
<th>CF4 (100% carbon tetrafluoride)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure of gas</td>
<td>1.0 Pa</td>
<td></td>
</tr>
<tr>
<td>Negative electric charge</td>
<td>1000 Hz, 10 μs</td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>60 minutes</td>
<td></td>
</tr>
<tr>
<td>Voltage</td>
<td>5 keV (Ti, SUS), 3 keV (PMMA)</td>
<td></td>
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</table>

X-ray photoelectron spectroscopy (XPS)

After fluorine ion implantation using CF4 gas, the surface of SUS was analyzed by means of X-ray photoelectron spectroscopy (XPS) (ESCA-1000AX, Shimadzu Co., Kyoto, Japan). Measurements were done using Mg Kα X-rays at 30 mA and 10 keV. Depth profile analysis was performed using Ar gas sputter method under these conditions: 20 mA current, 2 keV voltage, and gas pressure of 5×10⁻⁴ Pa. Sputtering speed was 20 Å (SiO2)/min. Binding energies were corrected against that of C 1s, an internal standard with binding energy at 285.0 eV.

Contact angle

After fluorine ion implantation by CF4 gas, the surface of SUS was washed in an ultrasonic bath (J.M. Ultrasonic Cleaner SUW-50D, J. Morita Co., Tokyo, Japan) containing distilled water for 10 minutes. After the washing procedure, the sample was dried at room temperature.

A drop of distilled water was carefully placed on each slightly dried, prepared surface, and contact angle was measured using the sessile drop technique with a contact angle meter (CA-DT, Kyowa Kaimen Kagaku Co. Ltd., Saitama, Japan). Five points per sample were measured. A total number of 10 samples were prepared for fluorine ion implantation (i.e., N=5) and to serve as controls with no ion implantation (i.e., N=5).

Fluoride ion release

Five SUS samples which were fluorine ion-implanted by CF4 gas were immersed in 10 ml of deionized water in a petri dish and shaken with a speed of 110 rpm (Double Shaker NR-3, Taitec Co., Saitama, Japan) at 37°C. The deionized water was changed every 24 hours and evaluated for fluoride ion concentration in ppm daily for a period of seven days. The immersion solution was kept at room temperature before fluoride ion concentration was measured. To provide a constant background ionic strength, 0.8 ml of total ionic strength adjustment buffer solution (TISABIII, Thermo Electron Co., Beverly, MA, USA) was added to 8 ml of immersion solution. Fluoride ion concentration (ppm) was then measured with an ion specific electrode (ionplus Sure-Flow Fluoride, 9609 BN, Orion Research Inc., Beverly, MA, USA) connected to an expandable ion analyzer (model 702A, Orion Research Inc., Beverly, MA, USA).
Calibration of the analyzer was performed before the test with standard solutions containing 0.1, 0.5, and 1.0 ppm of fluoride.

Microbiological examination
S. mutans (ATCC25175 type c, Summit Pharmaceuticals International Co., Tokyo, Japan) was used for the evaluation of bacterial adhesion and antibacterial activity. Substrate material was SUS which was fluorine ion-implanted by CF$_4$ gas.

Antibacterial activity
SUS was incubated at 37°C in 2 ml of BHI broth containing S. mutans with a cell density of 2×10$^7$ CFU/ml. After 48-hour incubation, 0.5 ml of solution was immediately added to 4.5 ml of PBS(-) and diluted. Following which, 100 μl of diluted solution was plated on BHI agar. After another 48 hours of incubation at 37°C, the number of colonies was counted. A total number of 20 samples were prepared for fluorine ion implantation (i.e., N=10) and to serve as controls with no ion implantation (i.e., N=10).

Initial adhesion
Into a petri dish were poured 20 ml of BHI broth and 200 μl of S. mutans with a cell density of 4×10$^8$ CFU/ml, and SUS material was placed with the fluorine ion-implanted surface upward. After 4-hour incubation at 37°C, the sample was removed from the petri dish and washed three times with phosphate buffered saline without calcium and magnesium (PBS(-)). The material was then placed in a tube containing 2 ml of PBS(-), and the tube was sonicated (Dentcraft Ultrasonic 3800N, Yoshida Co., Tokyo, Japan) for five minutes. The sample was removed from the tube, and 10 ml of BHI broth was added into the tube. After 24 hours of incubation at 37°C, 0.5 ml of solution was immediately added to 4.5 ml of PBS(-) and diluted. Following which, 100 μl of diluted solution was plated on BHI agar. After 48 hours of incubation at 37°C, the number of colonies was counted. A total number of 20 samples were prepared for fluorine ion implantation (i.e., N=10) and to serve as controls with no ion implantation (i.e., N=10).

RESULTS

Secondary ion mass spectrometry (SIMS)
Fig. 2 shows the peak counts of fluorine after ion implantation (N=4). In SUS and PMMA, ion implantation using CF$_4$ yielded significantly higher peak counts than Ar+F$_2$ (p<0.05 and p<0.001, respectively). But in Ti, there were no differences between Ar+F$_2$ and CF$_4$.

Concerning the role of Ar+F$_2$ as a fluorine-based gas for plasma-based ion implantation, it caused Ti substrate to yield a higher peak count than SUS and PMMA (p<0.05 and p<0.001, respectively), and SUS to be higher than PMMA (p<0.001). Similarly, with CF$_4$, the peak count of Ti was higher than that of SUS and PMMA (p<0.001), and SUS was higher than PMMA (p<0.001).

Fig. 3 shows the depth profiles until 10 counts of fluorine after ion implantation (N=4). As shown, it was only in PMMA that CF$_4$ led to a significantly higher depth profile than Ar+F$_2$ (p<0.001). With Ar+F$_2$ as a fluorine-based gas for ion implantation, Ti had a significantly higher depth profile than PMMA and SUS (p<0.001 and p<0.05, respectively). But with CF$_4$, PMMA was higher than SUS (p<0.05).

X-ray photoelectron spectrometry (XPS)
Figs. 4, 5, and 6 show the F 1s, Cr 2p$_{3/2}$, and Fe 2p$_{3/2}$ XPS spectra of SUS respectively. On the left side in each figure is the non-fluorine-ion-implanted control, while the right side shows the fluorine ion-implanted SUS substrate material. Table 2 lists the binding en-
Fig. 4  F 1s XPS spectra of SUS. Dashed lines show the peak position of F (685.5 eV).

Fig. 5 Cr 2p\textsubscript{3/2} XPS spectra of SUS. Dashed lines show the peak positions of metal Cr (574.3 eV), CrF\textsubscript{2} (578.2 eV), and Cr\textsubscript{2}O\textsubscript{3} (576.6 eV).

Fig. 6 Fe 2p\textsubscript{3/2} XPS spectra of SUS. Dashed lines show the peak positions of metal Fe (706.95 eV), FeF\textsubscript{2} (711.4 eV), and Fe\textsubscript{2}O\textsubscript{3} (710.9 eV).
ergies given in other published works. F 1s peak position was observed on the surface layer even after one minute of Ar gas sputtering (Fig. 4). Chemically shifted peaks of Cr 2p$_{3/2}$ were observed in the higher binding energy region on the surface and subsurface at one minute after sputtering (Fig. 5). As for the chemically shifted peak of Fe 2p$_{3/2}$, it was observed in the higher binding energy region in the surface layer (Fig. 6).

Table 2 Binding energies (eV) given in other published works

<table>
<thead>
<tr>
<th>Compound</th>
<th>Binding energy (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>685.5</td>
<td>Shimadzu Co.*</td>
</tr>
<tr>
<td>metal Cr</td>
<td>574.3</td>
<td>D. Briggs et al.*</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>576.6</td>
<td>D. Briggs et al.*</td>
</tr>
<tr>
<td>CrF$_2$</td>
<td>578.2</td>
<td>K. Hanamoto et al.*</td>
</tr>
<tr>
<td>metal Fe</td>
<td>706.95</td>
<td>D. Briggs et al.*</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>710.9</td>
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</tr>
<tr>
<td>FeF$_2$</td>
<td>711.4</td>
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</table>

*Shimadzu Co.: XPS Spectra Sequential Peak File

Contact angle
Fig. 7 shows the contact angles of SUS, where fluorine ion-implanted SUS surface showed a significantly higher contact angle than the non-fluorine-ion-implanted control ($p<0.001$).

Fluoride ion release
Fig. 8 shows the amount of fluoride ion release from the surface of fluorine ion-implanted SUS. A small amount of fluoride ions was released until the second day. After the third day, fluoride ion release ceased to be detected.

Antibacterial activity
Fig. 9 shows the S. mutans colonies on BHI agar for antibacterial activity evaluation, while Fig. 10 shows the CFU/ml values. It could be seen that fluorine ion-implanted SUS showed a lower CFU/ml value than the non-fluorine-ion-implanted control ($p<0.001$).

Initial adhesion
Fig. 11 shows the adhesion of S. mutans on the surface of SUS after four hours of incubation. Fluorine ion-implanted SUS showed less bacterial adhesion than the non-fluorine-ion-implanted control ($p<0.001$).
Affect the dose amount and implantation energy of compensation. The charge-up problem is expected to accumulation of implanted ions without any charge to a very high voltage owing to the positive charge of PMMA. In general, a polymer surface is charged than Ti and SUS. It might be due to the insulation ions implanted into PMMA was significantly lower materials, they were Ti, SUS, and PMMA.

This study, a mixed gas of 95\% argon and 5\% fluorine gas were used. As for substrate, they were Ti, SUS, and PMMA.

In the present study, the peak count of fluorine ions implanted into PMMA was significantly lower than Ti and SUS. It might be due to the insulation of PMMA. In general, a polymer surface is charged to a very high voltage owing to the positive charge accumulation of implanted ions without any charge compensation. The charge-up problem is expected to affect the dose amount and implantation energy of ions\(^ {25}\).

The peak count of fluorine ions implanted into Ti was the highest. However, the surface of Ti plate became discolored and corroded after plasma-based fluorine ion implantation. Oral prophylactic fluoride agents were reported to cause discoloration\(^ {26}\) and corrosion\(^ {27-30}\), as well as increase the fracture susceptibility of Ti\(^ {31}\). The corrosion resistance of Ti depends on the balance between the formation and dissolution of the passive oxide film. In general, Ti and its alloys are covered with a thin passive film (surface oxide film) consisting of low-crystalline or amorphous structure, and these films play a critical role in corrosion resistance\(^ {34,35}\). In particular, strong passive films are formed on the surface of Ti, which provide high corrosion resistance when subjected to hostile acidic environments and against various kinds of chemical agents\(^ {40}\). However, the presence of fluoride results in a low dissolved oxygen concentration, and thus hinders the formation of the passive film. It has been suggested that the corrosion of Ti occurs because the balance shifts to the dissolution reaction of the passive film\(^ {39}\). In the present study, the discoloration and corrosion further suggested that plasma-based fluorine ion implantation shifted the balance to dissolution of the passive film.

XPS analysis revealed that the binding energies of chromic oxide (Cr\(_2\)O\(_3\)) and chromic fluoride (CrF\(_2\)) were 576.6 eV\(^ {37}\) and 578.2 eV\(^ {38}\) respectively. Hence, the shifted peaks in the present study (Fig. 5) were due to Cr\(_2\)O\(_3\) and CrF\(_2\). The binding energies of iron fluoride (FeF\(_2\)) and iron oxide (Fe\(_2\)O\(_3\)) were reported to be 711.4 eV and 710.9 eV respectively\(^ {37}\), which meant that iron oxide (Fe\(_2\)O\(_3\)) was detected on the surface of fluorine ion-implanted SUS. However, on the surface and after one minute of sputtering, the peak was close to that of metal Fe. Compared with the non-fluorine-ion-implanted control, the spectra shifts were not changed. This finding thus suggested that fluorine did not react with Fe.

With regard to the effect on contact angle, that of fluorine ion-implanted SUS was significantly increased. As the contact angle increases, the wettability of the substrate decreases or that the latter becomes hydrophobic\(^ {29,30}\). It is known that organic polymers are generally hydrophobic as compared with inorganic materials (such as glass) and metals – which are hydrophilic. On the other hand, it has been found that adhesion of bacteria to materials is determined by the degrees of hydrophobicity of both bacteria and material surface\(^ {31,41,42}\). Dankert et al.\(^ {43}\) showed that a hydrophobic bacterium adhere to a hydrophobic surface more easily than its hydrophilic counterpart. According to interfacial thermodynamics, high surface free energy strains, such as S. mutans, should adhere preferentially to hydrophilic substrata. Riding on this hypothesis, it could thus be said that the decreased initial adhesion of S. mutans was

**DISCUSSION**

Dental appliances have complex shapes and surfaces. With plasma-based ion implantation, fluorine ions can be implanted not only into a plane surface, but also into a complex surface. However, fluorine gas is very dangerous. Therefore, fluorine-based gases such as CF\(_4\), C\(_2\)F\(_6\), SF\(_6\) or mixed gas of argon and F\(_2\) have been used for plasma-based ion implantation\(^ {24}\). In this study, a mixed gas of 95\% argon and 5\% F\(_2\) (Ar+F\(_2\)) and CF\(_4\) gas were used. As for substrate materials, they were Ti, SUS, and PMMA.

In the present study, the peak count of fluorine ions implanted into PMMA was significantly lower than Ti and SUS. It might be due to the insulation of PMMA. In general, a polymer surface is charged to a very high voltage owing to the positive charge accumulation of implanted ions without any charge compensation. The charge-up problem is expected to affect the dose amount and implantation energy of ions\(^ {25}\).

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mutans on the surface of fluorine ion-implanted SUS was due to the latter’s significantly increased contact angle.

With regard to fluoride release behavior, Verbeeck et al.\textsuperscript{19} reported that fluoride release from glass ionomer cements and composite resins occurred as two different processes. The first process was characterized by an initial burst of fluoride release, after which the release rate was markedly reduced and the release of fluoride continued for a long period of time. In the present study, a small amount of fluorine ions was released from the surface of fluorine ion-implanted SUS within 24 hours and an extremely small amount of fluorine ions was detected up to the second day. However, fluorine ions ceased to be detected after three days. According to our results, the maximum amount of fluoride ions released was about 0.03 ppm, and the detection limit of fluoride electrode in this study was 0.02 ppm. This finding thus suggested that there was no fluoride ion release from the surface of fluorine ion-implanted SUS.

With regard to the effect on bacterial adhesion, the fluorine ion-implanted SUS showed increased antibacterial activity. As a result, the initial adhesion of S. mutans on fluorine ion-implanted SUS decreased significantly compared with the non-fluorine-ion-implanted control. The decrease in initial adhesion in this study might be due to the increase of both contact angle and antibacterial activity of fluorine ion-implanted SUS. In an in vitro study\textsuperscript{18}, it was found that surface modification through a dry process—such as ion implantation—was useful in controlling the initial adhesion of oral bacteria, and that fluorine ion-implanted Ti surface exhibited antibacterial activity effectively against both P. gingivalis and A. actinomyctecomitans\textsuperscript{18}. Moreover, Li et al.\textsuperscript{19} also reported that cell attachment on PMMA surface could be controlled by fluorine ion implantation.

Two mechanisms of antibacterial action have been identified for fluorine ion-implanted materials. One mechanism of action is ascribed to the fluorine ions, while the other mode of action involves the formation of metal-fluoride complexes. Fluoride acts in multiple ways to affect bacterial metabolism in the mouth. For example, fluoride can act directly as an enzyme inhibitor to the glycolytic enzyme, enolase. On the other hand, metal-fluoride complexes are responsible for fluoride-induced inhibition of proton-translocating F-ATPases by mimicking phosphate to form complexes with ADP at the reaction centers of enzymes. ATPase plays an important role in the maintenance of intracellular pH by pumping out protons; inhibition of this enzyme disrupts the bacterial metabolism and aciduric capability of S. mutans\textsuperscript{20,15–40}. Based on the XPS spectra obtained, it could be seen that chromic fluoride complex was formed in fluorine ion-implanted SUS. Therefore, it was suggested that the possible antibacterial mechanism of fluorine ion-implanted SUS was caused by the formation of metal fluoride complexes.

CONCLUSIONS

Ti, SUS, and PMMA were materials implanted with fluorine ions in the surface and subsurface layers. For plasma-based fluorine ion implantation, CF$_4$ gas was found to be more suitable than Ar+P$_3$. First, XPS analysis of fluorine ion-implanted SUS showed the peaks of fluorine and chromic fluoride. Moreover, while the contact angle and antibacterial activity of fluorine ion-implanted SUS were significantly increased, the initial adhesion of S. mutans on the surface was significantly decreased. It was suggested that the decrease in S. mutans adhesion could be attributed to the increase of both contact angle and antibacterial activity. As for the antibacterial activity of fluorine ion-implanted SUS in this study, it most probably arose from the formation of metal-fluoride complexes, such as chromic fluoride. In summary, plasma-based fluorine ion implantation into dental materials could provide antibacterial activity and inhibit bacterial adhesion on the surface of dental materials.

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