Surface modification of stainless steel by plasma-based fluorine and silver dual ion implantation and deposition

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The aims of this study were to modify dental device surface with fluorine and silver and to examine the effectiveness of this new surface modification method. Stainless steel plates were modified by plasma-based fluorine and silver ion implantation-deposition method. The surface characteristics and brushing abrasion resistance were evaluated by XPS, contact angle and brushing abrasion test. XPS spectra of modified specimens showed the peaks of fluoride and silver. These peaks were detected even after brushing abrasion test. Water contact angle significantly increased due to implantation-deposition of both fluorine and silver ions. Moreover, the contact angle of the modified specimen was significantly higher than that of fluorine only deposited specimen with the same number of brushing strokes. This study indicates that this new surface modification method of fluorine and silver ion implantation-deposition improved the brushing abrasion resistance and hydrophobic property making it a potential antimicrobial device.

Keywords: Plasma-based ion implantation-deposition, Fluorine, Silver

INTRODUCTION

Bacterial colonization and subsequent device infection are common complications of medical and dental devices\(^1\). Metallic biomaterials such as stainless steel, titanium and titanium alloys are widely used in the fields of pedodontics, orthodontics, prostodontics, oral surgery and cardiovascular surgery. Medical and dental devices have complicated shapes and are susceptible to adhesion by bacteria resulting in dental caries\(^{2,6}\), periodontal disease\(^{7-9}\), or infection of soft oral tissue\(^{10}\). Moreover, oral bacteria can be released from dental plaque into salivary secretions and then aspirated into the lower respiratory tract causing pneumonia\(^{11,12}\). There is also evidence that periodontal infection with circulating antibodies against some oral pathogens increase the risk for stroke and cardiovascular disease\(^{13,14}\). Also, biomedical-related infections often require device removal and replacement and immediate aggressive antibiotic therapy to avoid the development of severe complications. Consequently, additional treatment greatly increases patient’s discomfort and treatment costs\(^{15,16}\). Considering all these, it is therefore important to inhibit the adhesion of oral bacteria on exposed device surfaces in the oral cavity to keep them plaque-free.

Device surface modifications are generally classified into physical and chemical modifications. In the case of metallic materials, physical modifications are mainly chosen. For instance, several studies have indicated that surface modifications, such as ion implantation\(^{17,21}\) and film coating\(^{7,22}\), are effective in reducing bacterial infection. Plasma-based ion implantation (PBII) in particular, is a promising method for the surface modification of three-dimensional materials\(^{23}\). In the PBII, the samples are surrounded by high-density plasma and pulse-biased to a high negative potential relative to the chamber wall. Ions generated in the overlying plasma accelerate across the ion sheath formed around the samples and are implanted into their surfaces\(^{24}\). For example, a sample possessing a complicated shape can be treated with good conformity and uniformity without beam scanning and special target manipulation. In addition, the use of multiple processes, such as simultaneous and consecutive ion implantation-deposition, and etching, are possible by varying the instrumental parameters without breaking vacuum. In particular, the ion deposition with simultaneous ion implantation (plasma-based ion implantation and deposition: PBII-D) is desirable for efficient processing and has an advantage over conventional methods\(^{25}\).

Recently, several researchers have carried out surface modification using fluorine (F) ion and found it to be a useful means of inhibiting bacterial adhesion\(^{17,18,20,22,26}\). In our previous study, stainless steel implanted with F ion by PBII could provide antibacterial activity and inhibit bacterial adhesion\(^{20}\). It was suggested that the effects could be attributed to the increased contact angle and existence of metal-fluoride complexes on the surface of the F implanted stainless steel. In the PBII-D, since both processes of ion implantation and deposition are done simultaneously, it was anticipated that required ions existed more on the surface of the materials. In addition, it is well known that silver (Ag) possesses antibacterial property without any toxic effects in comparison to other heavy metal ions. Therefore, Ag is the first candidate used in antibacterial research. Several reports have indicated an effective treatment to reduce bacterial infection based on the Ag zone near the surface of biomaterials\(^{17,19,27-29}\). In the dental field, agents and materials containing both F and Ag, such as diammine silver fluoride solution\(^{30}\) for inhibition of
caries progress and silver glass ionomer cement\textsuperscript{31} for filling or lining of cavities, are widely used. However, there have been no known reports on device surface modification using both F and Ag.

We then developed the new technique to simultaneously implant and deposit both F and Ag ions into stainless steel using PBII-D for the first time. The aim of this study was to examine the effectiveness of F and Ag implanted-deposited into stainless steel by evaluating the surface characteristics and brushing abrasion resistance.

**MATERIALS AND METHODS**

*Plasma-based F and Ag ion implantation-deposition*

Stainless steel 316L plates (composition in wt%: C=0.12, Si=0.48, Mn=0.84, P=0.27, S=0.02, Ni=12.02, Cr=17.42, Mo=2.03, Fe=balance; Nippon Steel & Sumikin Stainless Steel Co., Tokyo, Japan) with measurements of 10 mm × 10 mm × 1 mm were used. The stainless steel plates were polished mechanically to a mirror finish and washed in an ultrasonic bath with 98% ethanol. The stainless steel plates were then modified by plasma-based ion implantation-deposition equipment at Plasma Ion Assist Co., Ltd., Kyoto, Japan. A schematic diagram of both F and Ag ion implantation-deposition method by PBII-D is illustrated in Fig. 1. Fluoride gas used for F ion implantation-deposition was octafluoropropane (C\textsubscript{3}F\textsubscript{8}). For the Ag ion implantation-deposition, a 99.8% Ag mesh was set 10 mm above the stainless steel plates and sputtered by C\textsubscript{3}F\textsubscript{8} gas. The conditions of plasma-based F and Ag ion implantation-deposition are shown in Table 1. The stainless steel plates were grouped into: control group, those that were not treated with any ion; F deposited group, those that were deposited with F ion; and F+Ag implanted-deposited group, those that were implanted-deposited with both F and Ag ions.

*Surface analysis by XPS*

The surfaces of the control, F deposited and F+Ag implanted-deposited stainless steel were characterized by X-ray photoelectron spectroscopy (XPS). XPS spectra were obtained using an X-ray photoelectron spectrometer (ESCA-1000AX, Shimadzu Co., Kyoto, Japan) with Mg-K\textalpha radiation operated at 30 mA current and 10 kV accelerating voltage. Specifically, depth profile analysis for the F+Ag implanted-deposited stainless steel was performed using Ar etching at 20 mA current and 2 kV voltage under the pressure of 5×10\textsuperscript{-4} Pa. The Ar etching rate was approximately 2 nm/min on Al\textsubscript{2}O\textsubscript{3}. The binding energies obtained by XPS were corrected against that of C1s, an internal standard with binding energy at 285.0 eV for the C-C and C-H (saturated hydrocarbons)\textsuperscript{32}.

*Contact angle measurements*

Samples were washed in ultrasonic bath (J.M. Ultrasonic Cleaner SUW-50D, J. Morita Co., Tokyo, Japan) containing distilled water for 10 minutes, and then dried at room temperature. Static contact angle measurements were conducted by the sessile drop technique using a contact angle meter (CA-DT, Kyowa Kaimenkagaku Co. Ltd., Saitama, Japan) with distilled water. Ten points per group were measured.

*Brushing abrasion test*

The brushing abrasion test machine (MANA-63S, MASUDA Co., Osaka, Japan) was used. A commercial toothbrush (Dr. Bee Young II soft, Bee Brand Medico Dental Co., Ltd., Osaka, Japan) was attached to the toothbrush holder in contact with the F deposited and F+Ag implanted-deposited stainless steel set on the sample holder. Distilled water without dentifrice was

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**Table 1** Experimental groups and specific condition for fluorine and silver ion implantation-deposition into the surfaces of stainless steel plates

<table>
<thead>
<tr>
<th>Group</th>
<th>Fluorine treatment</th>
<th>Silver mesh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>F deposited</td>
<td>C\textsubscript{3}F\textsubscript{8}</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td>−0.5 kV / 60 min</td>
<td>Used</td>
</tr>
<tr>
<td>F+Ag implanted-deposited</td>
<td>C\textsubscript{3}F\textsubscript{8}</td>
<td>C\textsubscript{3}F\textsubscript{8}</td>
</tr>
<tr>
<td></td>
<td>−5 kV / 30 min + −0.5 kV / 60 min</td>
<td>Used</td>
</tr>
</tbody>
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![Fig. 1 Schematic presentation of Plasma-based F and Ag ion implantation-deposition technique.](image-url)
then poured into the vessel, and the machine was run at 80 rpm with a 200 g load. The contact angle measurements of the F deposited and F+Ag implanted-deposited stainless steel were done every 10,000 strokes up to 60,000 strokes. In the control stainless steel, the contact angle was measured without brushing. Five points per group were measured. Furthermore, XPS analysis of the F+Ag implanted-deposited stainless steel was done every 10,000 strokes up to 60,000 strokes.

Statistical analysis

The results of the contact angle measurements before and after the brushing abrasion test were expressed as the mean ± standard deviation. The data were analyzed using one-way ANOVA and Tukey’s multiple comparison tests (α = 0.05).

RESULTS

XPS analysis

1. XPS analysis before brushing

1.1 Wide-scan XPS analysis

XPS wide-scan spectra of the surfaces of the control (a), F deposited (b) and F+Ag implanted-deposited (c) stainless steel are shown in Fig. 2. The elements C, O, Cr, Fe, Ni and Mo were detected in the wide-scan spectrum of the control stainless steel (Fig. 2a). F1s peak appeared on the F deposited stainless steel surface (Fig. 2b), and both F1s and Ag3d peaks appeared on the F+Ag implanted-deposited stainless steel surface (Fig. 2c). In the F deposited and F+Ag implanted-deposited stainless steel, F1s spectra were divided into the two regions (Figs. 2b and 2c).

1.2 Narrow-scan XPS analysis

Fe2p3/2, Cr2p3/2 and F1s XPS narrow-scan spectra of the control (a), F deposited (b) and F+Ag implanted-deposited (c) stainless steel are shown in Fig. 3. In Fe2p3/2 spectra for the control stainless steel surface, several peaks at 710-711.5 eV and 707.5 eV were detected. These peaks energies were approximated to iron oxides. Chemical shifts of Fe2p3/2 spectra were observed in the higher binding energy region (711.8 eV) in the F deposited and F+Ag implanted-deposited stainless steel. It was suggested that the shifted peak energy approximated to iron fluoride (FeF3) (711.4 eV). Cr2p3/2 peak position of the control stainless steel was detected at chromium oxide (Cr2O3) (576.8 eV). Chemical shifts of Cr2p3/2 spectra were observed in the higher binding energy region in the F deposited and F+Ag implanted-deposited stainless steel. This suggested that the shifted peak energy was approximated to chromium fluoride binding energy (578.1 eV). Ag3p3/2 signal appeared at 573.2 eV on the surface of the F+Ag implanted-deposited stainless steel. On the surfaces of the F deposited and F+Ag implanted-deposited stainless steel, F1s signal was divided into two peak positions. The peak at 685.0 eV was approximated to the metal-fluoride bonding state. Another peak energy was approximated to the carbon-fluoride binding energy, such as p-(CF2-CF2) at 689 eV. The F-Ag bonding state was not detected.

Fig. 2 XPS wide-scan spectra of the control (a), F deposited (b) and F+Ag implanted-deposited (c) stainless steel. Dashed lines indicate the peak positions of stainless steel’s components. Black triangles indicate the peak positions of implanted F and Ag.
1.3. Depth profile of the F+Ag deposited stainless steel
The F1s and Ag3d XPS depth profiles of the F+Ag implanted-deposited stainless steel are shown in Fig. 4. After 0.5 minutes of etching by Ar gas, the peak at 689.0 eV (the carbon-fluoride bonding state; shown in Fig. 3) disappeared and the peak at 685.0 eV (the metal-fluoride bonding state; shown in Fig. 3) was observed maximally. Furthermore, the metal-fluoride peak decreased as the Ar etching increased, and was not detected after 2.0 minutes of Ar etching. In addition, the peak at 690-691 eV in F1s region was also detected in the depth profile of the control stainless steel. Thus, the peak is not dependent on the presence of fluoride. Ag3d signal decreased with depth. However,

Fig. 3  Fe2p3/2, Cr2p3/2 and F1s XPS narrow-scan spectra of the control (a), F deposited (b) and F+Ag implanted-deposited (c) stainless steel. Dashed lines indicate the peak positions of Fe (707.5 eV) and FeF2 (711.8 eV) in the Fe2p3/2 region, Ag3p3/2 (573.2 eV), Cr2O3 (576.8 eV) and CrF2 (578.1 eV) in the Cr2p3/2 region, F (685.0 eV) and p-(CF2=CF2) (689.0 eV) in F1s region. The horizontal bar indicates the peak position of iron-oxide.

Fig. 4  F1s and Ag3d XPS depth profiles of the F+Ag implanted-deposited stainless steel. Dashed lines indicate the peak positions of metal-fluoride (685.0 eV) and p-(CF2=CF2) (689.0 eV) in the F1s region, and Ag (368.1 eV) in the Ag3d region.
Fig. 5  Cr2p₃/₃ and F1s XPS profiles of the F+Ag implanted-deposited stainless steel before/after the brushing abrasion test. Dashed lines indicate the peak positions of Ag3p₃/₃ (573.2 eV), Cr₂O₃ (576.8 eV) and CrF₂ (578.1 eV) in the Cr2p₃/₃ region, and F (685.0 eV) and p-(CF₂-CF₂) (689.0 eV) in the F1s region.

Ag was detected after Ar etching for 4.5 minutes in Ag3d depth profile.

2. XPS analysis of the F+Ag deposited stainless steel after the brushing abrasion test
Cr2p₃/₃ and F1s XPS narrow-scan spectra of the F+Ag implanted-deposited stainless steel surface before and after the brushing abrasion test are shown in Fig. 5. Ag3p₃/₃ peak area at 573.2 eV in Cr2p₃/₃ region decreased with the increase in brushing strokes. However, Ag3p₃/₃ peak area was still detected after 60,000 strokes brushing. Similarly, the decreased carbon-fluoride bonding state in 688-689 eV after brushing was visible in F1s region spectra. The peak of the carbon-fluoride bonding state was not detected after 60,000 brushing strokes. Nevertheless, the peak of metal-fluorides was detected even after 60,000 brushing strokes.

Contact angle measurements
The typical water drop pictures on the control, F deposited and F+Ag implanted-deposited stainless steel plates before the brushing abrasion test, and contact angle values of the F deposited and F+Ag implanted-deposited stainless steel before and after the brushing abrasion test are shown and compared to that of the control without the brushing abrasion test in Fig. 6. The contact angles of the F deposited and F+Ag implanted-deposited stainless steel were significantly higher than that of the control stainless steel (p<0.001). Moreover, the contact angle of the F+Ag implanted-
deposited stainless steel was higher than that of the F deposited stainless steel ($p<0.001$). In the F deposited stainless steel, the contact angles after 10,000, 30,000 and 60,000 brushing strokes were significantly lower than before brushing (10,000 and 30,000 strokes $p<0.05$, 60,000 strokes $p<0.001$). Particularly, there was no significant difference in the contact angle between the F deposited stainless steel after 30,000 and 60,000 brushing strokes and the control stainless steel. The F deposited and F+Ag implanted-deposited stainless steel exhibited a similar pattern in the contact angle after the brushing abrasion test; that is, the contact angles of the F+Ag implanted-deposited stainless steel after 10,000, 30,000 and 60,000 brushing strokes were significantly lower than before brushing (10,000 strokes $p<0.01$, 30,000 and 60,000 strokes $p<0.001$). However, the F+Ag implanted-deposited stainless steel after the brushing abrasion test resulted in a significantly higher contact angle compared to the control stainless steel (10,000, 30,000 and 60,000 strokes $p<0.001$). Moreover, the contact angle of the F+Ag implanted-deposited stainless steel was significantly higher than the F deposited stainless steel for the same number of brushing strokes (10,000 strokes $p<0.01$, 30,000 strokes $p<0.05$, 60,000 strokes $p<0.001$).

**DISCUSSION**

In the present study, both F and Ag ions were simultaneously implanted-deposited into stainless steel (SUS 316L) using the PBI-D with silver mesh and were examined for effectiveness by evaluating the XPS spectra and the contact angles. One of the austenitic stainless steels, SUS 316L, has long been used in orthopedic implants for fracture fixation and joint replacement. Because this type of stainless steel has also been used in dentistry for orthodontic appliances and preformed crowns for primary teeth restoration, it was chosen in the present study.

Based on the results of the XPS analyses, it was obvious that there was indeed F and Ag on the surface of the F+Ag implanted-deposited stainless steel (Fig. 2). Further, the results suggested that F combined with carbon from the C$_2$F$_8$ gas and with metallic elements from the stainless steel substrate (Fig. 3). The carbon-fluoride bonding state on the surface disappeared after Ar etching for 0.5 minutes to a depth of about 1 nm. While the metal-fluoride complexes were dominant inside the F+Ag implanted-deposited stainless steel after Ar etching for 2.0 minutes, to a depth of about 4 nm (Fig. 4). The metal-fluoride complexes are also responsible for fluoride inhibition of proton-translocating F-ATPases and are thought to mimic phosphate to form complexes with ADP at the reaction center of enzymes. Indeed, ATPase plays an important role in the maintenance of intracellular pH by pumping out protons and in the inhibition of the enzyme that disrupts the bacterial metabolism and acidic capability of Streptococcus mutans.$^{[17,36-38]}$

Several related researches have indicated effective treatments to reduce bacterial infection based on the Ag zone near the surface of biomaterials.$^{[19,27-29]}$ In this study, the F+Ag implanted-deposited stainless steel had the metal-fluoride complexes and Ag near the surface. Therefore, this F+Ag implanted-deposited stainless steel was expected to be effective in promoting surface antibacterial activity. This is best to be confirmed in future studies.

Oka et al.$^{[30]}$ discussed the microstructure in nano-interface between an aluminum alloy substrate and a diamond-like carbon (DLC) film prepared by PBII-D, showing the formation of the mixing layer which was constructed by the implanted ions and the substrate elements. In the F+Ag implanted-deposited stainless steel, the results of XPS spectra suggested that the deposited layer had the carbon-fluoride bonding state from the C$_2$F$_8$ gas plasma, metal-fluorides and Ag, and the mixing layer formed by metal-fluorides and Ag. In Figure 4, it was shown that the carbon-fluoride bonding state disappeared after 0.5 minutes of Ar etching (etching speed; approximately 2 nm/min on Al$_2$O$_3$) in the F+Ag implanted-deposited stainless steel which may indicate that the carbon-fluoride deposited layer was less than 1 nm in depth. After 60,000 brushing strokes, the carbon-fluoride almost disappeared on the surface of the F+Ag implanted-deposited stainless steel (Fig. 5), suggesting that the deposited layer could last until 60,000 brushing strokes. The Ag3p (573.2 eV) peak and the F1s peak (685.0 eV) from metal-fluoride complexes were still visible on the surface of the F+Ag implanted-deposited stainless steel even after 60,000 brushing strokes (Fig. 5), suggesting that the mixing layer could resist more than 60,000 brushing strokes. Kanter et al.$^{[40]}$ estimated that 20,000 brushing strokes were the equivalent to approximately 5 years of brushing. The present study confirmed that the mixing layer of the F+Ag implanted-deposited stainless steel could withstand brushing for more than 15 years, and Ag could withstand 60,000 brushing strokes or the equivalent of 15 years of brushing with a toothbrush.

The contact angle is characteristic of the surface energy of a solid surface, and has been used for determining the wettability and hydrophobic property of various solid materials. Several reports showed that bacterial adhesion decreased with the increasing contact angle of the solid surfaces and the decreasing surface energy of the substrate surfaces.$^{[18,20,41,42]}$ Some research found that bacteria adhered to the hydrophobic materials could be more easily removed by an air-bubble jet.$^{[53,44]}$ It was also reported that there exists direct the relationship between the contact angle and the antibacterial property of various fluoride-implanted stainless steel.$^{[18,20]}$ In this study, the contact angle of the F+Ag implanted-deposited stainless steel (101.9±1.4°) was higher than those of the modified stainless steel in previous studies (Chao et al.$^{[18]}$; 33.3±0.1° and Nurhaerani et al.$^{[20]}$; approximately 90°). In addition, the contact angle of the F+Ag implanted-deposited stainless steel after the brushing abrasion
test was significantly higher than that of the control stainless steel (Fig. 6). Furthermore, contact angle of the F+Ag implanted-deposited stainless steel was significantly higher than the F deposited stainless steel with the same number of brush strokes. This suggested that the brushing abrasion resistance of the deposited or mixing layer could be improved, and the hydrophobic property would remain after brushing. However, it was thought that decrease of contact angle after 10,000 brushing strokes in each sample group may be affected by change of the surface morphology. This is also best to be confirmed in future studies.

Compared to conventional ion implantation method, PBII-D equipment is smaller, less expensive, simpler to maintain and operate, and more compatible with “in-house operation” as opposed to the “outside service facility mode operation” which is prevalent in the present in the ion beam processing industry. This new technology can be used to deposit F and Ag on stainless steel dental devices during periodic dental appointments. Because PBII-D process can operate under lower temperature than conventional ion implantation methods, the deformation of stainless steel devices can even be minimized.

CONCLUSION

In this study, stainless steel plates were implanted-deposited with F and Ag ions simultaneously by a hybrid process of the PBII-D. The F+Ag implanted-deposited stainless steel obtained the hydrophobic property and the existence of carbon-fluoride complexes, metal-fluoride complexes and Ag on the surface was confirmed. Moreover, due to the presence of both F and Ag ions, the brushing abrasion resistance of the deposited or mixing layer was improved, and the hydrophobic properties remained even after brushing with a toothbrush. These results suggested that the new surface modification method of simultaneous F and Ag ion implantation-deposition by PBII-D could provide possible antimicrobial properties to medical and dental devices.

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