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学位論文

The Study of Plasma Based Fluorine Ion Implantation into Dental Materials for Inhibition of Bacterial Adhesion

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Keywords：Dental materials, Fluorine ion, Plasma based ion implantation, Inhibition of bacterial adhesion

Abstract：The purposes of the present study were to evaluate the profile and spectra of dental materials modified by plasma based fluorine ion implantation into the surface of dental materials and to evaluate the effects of fluorine ion implantation on the contact angle, surface roughness, fluorine ion release and bacterial adhesion. The dental materials used for evaluation were pure titanium, stainless steel SUS316L and polymethyl methacrylate. Fluorine gases for plasma based ion implantation were $Ar+F_2$ (95% argon and 5% F_2) and CF_4.

The results were as follows:

1. The peak count of fluorine ion implanted into polymethyl methacrylate was significantly lower than titanium and stainless steel. The peak count of fluorine in titanium was higher than stainless steel and polymethyl methacrylate, but the surface of titanium discolored, might be corrosion, after plasma based fluorine ion implantation.
2. The depth of fluorine ion implantation by CF_4 gas into stainless steel was 173.3 ± 144.8 nm in SIMS analysis and until second layer (1.0 minute argon gas sputtering) in XPS analysis.
3. XPS spectra of fluorine ion implanted stainless steel showed peaks of fluorine and chromic fluoride.
4. Fluorine ion implantation into stainless steel significantly increased contact angle, but did not change surface roughness.
5. A small amount of fluorine ion released from the surface of the fluorine ion implanted stainless steel until 48 hours immersion in deionized water. Fluorine ion might not release from the inside but from the fluorine ion contaminated surface.
6. Initial 4 hours adhesion of *S. mutans* on the surface of fluorine ion implanted stainless steel significantly decreased compared with fluorine ion non-implanted control. Long-term 7 days and 21 days adhesion did not change compared with fluorine ion non-implanted control.
7. The fluorine ion implanted stainless steel showed significantly lower number of CFU, i.e., significantly higher antibacterial activity.

It was concluded that the plasma based fluorine ion implantation into the dental materials could inhibit bacterial adhesion on the surface of the dental materials.

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INTRODUCTION

In a dental clinic, various kinds of appliances such as space maintainer and space regainer for occlusal guidance, orthodontic appliance, denture and others are used frequently for children and adults. These appliances are apt to adhere oral bacteria[1-6] and to cause dental caries[7, 8], periodontal disease or inflammation of oral soft tissue[9, 10]. Prevention of these secondary diseases caused by oral appliances is very important for quality of all life stages and for restraint of increase of dental expenses.

Plasma surface modification as an economical and effective material processing technique is gaining popularity in the biomedical field. It is possible to change continuum of the chemical composition and properties such as wettability, adhesion, dyeability, refractive index, hardness, chemical inertness, lubricity and biocompatibility of material surfaces[11]. In the recent years, plasma based ion implantation has become a great interest for modify the surfaces of biomaterials[12, 13]. In plasma based ion implantation, the materials are immersed in plasma and surrounded by 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 materials and implanted into the surface of the materials. Compared to conventional ion implantation, the plasma based ion implantation facility 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 at present in the ion beam processing industry[13-17]. Some researchers carried out the surface modification by ion implantation. However, they mostly concentrated on the corrosion, wear and fatigue resistance properties of titanium (Ti). Several research groups improved the biocompatibility by implanting Ca^{2+} and Mg^{2+} into Ti and alumina, respectively[17].

In this study, the surface of Ti, stainless steel (SUS) and polymethyl methacrylate (PMMA) were modified by plasma based fluorine (F) ion implantation for the inhibition of oral bacterial adhesion. Ti, SUS and PMMA are frequently used materials in dentistry. Ti is used on several dental applications, such as dental implants, removable and fixed partial dentures. The use of Ti has increased due to their excellent biocompatibility, high strength to weight ratio and corrosion-resistance[18, 19]. SUS is also used materials in dentistry for occlusal guidance, orthodontic treatment, tooth and alveolar bone fracture fixation devices and implant [20-23]. In pediatric dentistry, SUS crown has been shown to provide the most durable restorative material for primary molars[24-27]. PMMA is used in wide variety in dental applications such as for denture bases[28] and bone cement for the fixation of total hip prostheses[29]. Fluoride is widely used as a highly effective anti-caries agent. Fluoride is able to act directly to bacteria as an enzyme inhibitor, and another mode of action to bacteria involves the formation of metal-fluoride complexes[30, 31].

Bacterial adhesion to biomaterial surface is an important step in the pathogenic infection. Bacterial adhesion is very complicated process that is affected by many factors, such as the environmental factors (temperature, time period of exposure and bacterial concentration), the bacterial characteristics (bacterial hydrophobicity and bacterial surface charge) and the surface characteristics of the biomaterials (chemical composition, surface charge, hydrophobicity and surface roughness)[32]. The formation of superficial biofilm on the dental materials is a complex phenomenon and the different key factors are involved. There are at least two methods for inhibiting the formation of microbial plaque[33]. The first method is to inhibit the initial adhesion of oral bacteria. The second method is to inhibit the colonization of oral bacteria which involves surface antibacterial activity[31].

The purposes of this study were to evaluate the profile and spectra of F ion implantation into the surface of dental materials and to evaluate the effects of F ion implantation on the contact angle, surface roughness, F ion release and the bacterial adhesion.

MATERIALS AND METHODS

A. Plasma based fluorine ion implantation

The principle of plasma based ion implantation is shown in Figure 1 (modified from Okui *et al.*[34]). The material is surrounded by high density plasma and is pulse-biased to a high negative potential relative to the chamber wall. Ions generated in the overlying plasma are accelerated across the sheath which is formed around the material and is implanted into the surface of the material.

Ti, SUS and PMMA plates with size 10×10×1 mm were

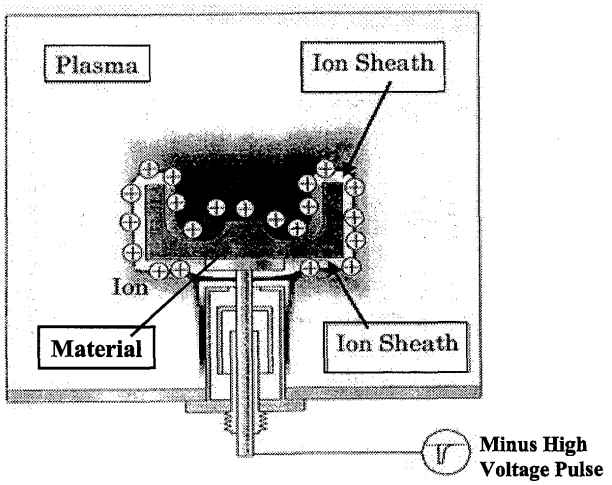

Fig. 1 Principle of plasma based ion implantation

modified by plasma based ion implantation in Ion Engineering Research Institute Co., Osaka, Japan. Ti (TP340C, titanium 99.98wt%, H 0.003wt%, O 0.09wt%, N 0.01wt%, Fe 0.07wt%) was produced by Kobe Steel, Ltd., Kobe, Japan. SUS (SUS316L, Fe 65.67wt%, Cr 17.00wt%, Ni 13.00wt%, Mo 2.40wt%, Mn 1.40wt%, C 0.03wt%, Si 0.50wt%) was produced by Daido Steel Co., Ltd., Nagoya, Japan. PMMA (ACRYPET VH#001) was produced by Mitsubishi Rayon Co., Ltd., Tokyo, Japan. F gas for plasma based ion implantation were mixed gas of 95% argon and 5% F_2 ($Ar+F_2$) or 100% carbon tetra fluoride (CF_4) gas. The condition of plasma based F ion implantation is shown in Table 1. As a control, F ion non-implanted Ti, SUS and PMMA were used.

B. Profile and spectra of fluorine ion implantation

1) Secondary ion mass spectrometry (SIMS)

The peak count (count per second, CPS) and the depth until 10 counts (nm) of F ion implantation into Ti, SUS and PMMA were measured with secondary ion mass spectrograph (ADEPT 1010, ULVAC Inc., Kanagawa, Japan). Sputtering ion for measurement was 3.0 keV Cs^+. The numbers of $Ar+F_2$ gas implanted material and CF_4 gas implanted material were four, respectively.

2) X-ray photoelectron spectroscopy (XPS)

SIMS analysis showed that the peak count of F ion implanted into PMMA was very small, the implanted Ti had discoloration and corrosion and that CF_4 gas was more suitable than $Ar+F_2$ gas. Therefore, the XPS analysis and the following experiments were done by using only SUS with CF_4 gas.

The surface of SUS which was F ion implanted by CF_4 gas was analyzed with an XPS (ESCA-1000AX, Shimadzu Co., Kyoto, Japan). Measurements were done using Mg Kα X-ray under condition of 30 mA and 10 keV. Depth analysis was done by Ar gas sputtering under condition of 20 mA and 2 keV. Sputtering speed was 20 Å (SiO_2)/minute.

C. Contact angle

The SUS which was F ion implanted by CF_4 gas was washed in an ultrasonic bath (J.M. Ultrasonic Cleaner SUW-50D, J. Morita Co., Tokyo, Japan) containing distilled water for 10 minutes. After washing procedures, the material was dried in room temperature.

Contact angle for distilled water was measured with a contact angle meter (CA-DT, Kyowa Kaimenkagaku Co., Ltd., Saitama, Japan). Five points per one material were measured. The numbers of F ion implanted materials and F ion non-implanted control were five, respectively.

Table 1. Condition of F ion implantation into surface of dental materials

Gas	**$Ar+F_2$ (95% argon and 5% fluorine)** **CF_4 (100% carbon tetra fluoride)**
Pressure of gas	**1.0 Pa**
Negative electric charge	**1000 Hz, 10 μs**
Time	**60 minutes**
Voltage	**5 keV (Ti, SUS), 3 keV (PMMA)**

D. Surface roughness

The SUS which was F ion implanted by CF_4 gas was washed in an ultrasonic bath (J.M. Ultrasonic Cleaner SUW-50D, J. Morita Co., Tokyo, Japan) containing distilled water for 10 minutes. After washing procedures, the material was dried in room temperature.

The surface of SUS was scanned by using stylus profilometer (Talyscan, Rank Taylor Hobson Ltd., Leicester, UK) and the surface roughness was analyzed by using three-dimensional analysis software (Talymap 3D Analysis Software, Rank Taylor Hobson Ltd., Leicester, UK). Five scans per one material were done. The numbers of F ion implanted materials and F ion non-implanted control were five, respectively.

Surface topography of the material was observed by using a scanning electron microscope (SEM) (JSM 5300, JEOL Ltd., Tokyo, Japan).

E. Fluorine ion release

Five SUS materials which were F ion implanted by CF_4 gas were immersed in 10 ml deionized water in a petri dish and shaken with a speed of 110 rpm (Double Shaker NR-30, Taitec Co., Saitama, Japan) at 37℃. The deionized water was changed every 24 hours and evaluated for F ion concentration in ppm daily till 7 days.

The material immersed solution was kept at room temperature before the F ion concentration was measured. To 8 ml of material immersed solution, 0.8 ml total ionic strength adjustment buffer solution (TISAB III, Thermo Electron Co., Beverly, MA, USA) was added to provide a constant background ionic strength. F ion concentration (ppm) was 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 720A, Orion Research Inc., Boston, MA, USA). Calibration of the analyzer was performed before the testing with standard solution of 0.1, 0.5 and 1.0 ppm F ion.

F. Bacterial adhesion

S. mutans (ATCC 25175 type c, Summit Pharmaceuticals

International Co., Tokyo, Japan) was used for the evaluation of bacterial adhesion and antibacterial activity. The material was SUS which was F ion implanted by CF_4 gas.

1) Initial adhesion

Into a petri dish, 20 ml of BHI broth and 200 μl of *S. mutans* with concentration 4×10^8 CFU/ml were poured and SUS was placed with the F ion implanted surface upward. After 4 hours incubation at 37℃, the material 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 5 minutes. The material was removed from the tube and 10 ml of BHI broth was added into the tube. After 24 hours incubation at 37℃, 0.5 ml of solution was immediately transferred into 4.5 ml of PBS (-) and diluted. 100 μl of diluted solution was plated on BHI agar. After 48 hours culture at 37℃, the number of colonies was counted. The numbers of F ion implanted material and F ion non-implanted control were ten, respectively.

2) Long-term adhesion

Back and lateral side of SUS were covered with hydrophilic vinyl polysiloxane impression material (Exafine regular hard type and putty type, GC Co., Tokyo, Japan) for the prevention of *S. mutans* adhesion. The material was hanging with orthodontic 0.9 mm wire (Sun-Platinum Orthodontic Wires, Dentsply-Sankin Co., Tokyo, Japan) and then four materials were incubated at 37℃ in 200 ml of BHI broth containing 5% sucrose and *S. mutans* with concentration 3×10^7 CFU/ml. The medium was changed every 24 hours. After 7 and 21 days incubation, the cover of the impression material was removed and the material was washed three times with deionized water. The material was fixed with 99.5% ethanol and dried for 24 hours at 37℃. The weight of the material was measured (CP225D, Sartorius AG, Goettingen, Germany) before and after incubation. Difference of weight between before and after incubation was calculated. The numbers of F ion implanted material and F ion non-implanted control were ten, respectively.

3) Antibacterial activity

SUS was incubated at 37℃ in 2 ml of BHI broth containing *S. mutans* with concentration 2×10^7 CFU/ml. After 48 hours incubation, 0.5 ml of solution was immediately transferred into 4.5 ml of PBS (-) and diluted. 100 μl of diluted solution was plated on BHI agar. After 48 hours culture at 37℃, the number of colonies was counted. The numbers of F ion implanted material and F ion non-implanted control were ten, respectively.

G. Statistical analysis

The statistical analysis was performed with Student's *t*-test using computer software (SPSS 10.0 for windows, SPSS Japan Inc., Tokyo, Japan).

RESULTS

A. Profile and spectra of fluorine ion implantation

1) SIMS analysis

The profile of F ion implantation by CF_4 gas into Ti, SUS and PMMA is shown in Figure 2. The peak counts of Ti, SUS and PMMA were 654,000, 257,000 and 2,970 CPS, respectively. The depth until 10 counts of Ti, SUS and PMMA were 400, 113 and 457 nm, respectively.

The peak counts of F ion implantation (N=4) are shown in Table 2 and Figure 3. In SUS and PMMA, CF_4 was significantly higher than $Ar+F_2$ ($p<0.05$ and $p<0.001$, respectively). But in Ti, there was no difference between $Ar+F_2$ and CF_4. Concerning about $Ar+F_2$, Ti was higher than SUS and PMMA ($p<0.05$ and $p<0.001$, respectively), and SUS was higher than PMMA ($p<0.001$). Concerning about CF4 also, Ti was higher than SUS and PMMA ($p<0.001$), and SUS was higher than PMMA ($p<0.001$).

The depth until 10 counts of F ion implantation (N=4) is shown in Table 3 and Figure 4. Only in PMMA, CF_4 was significantly higher than $Ar+F_2$ ($p<0.001$). Concerning about $Ar+F_2$, Ti was higher than PMMA and SUS ($p<0.001$ and $p<0.05$, respectively). Concerning about CF_4, PMMA was higher than SUS ($p<0.05$).

2) XPS analysis

F 1s, Cr $2p_{3/2}$ and Fe $2p_{3/2}$ XPS spectra of SUS are shown in Figure 5. Left side is F ion non-implanted control and right side is F ion implanted material. Binding energy by other works is shown in Table 4.

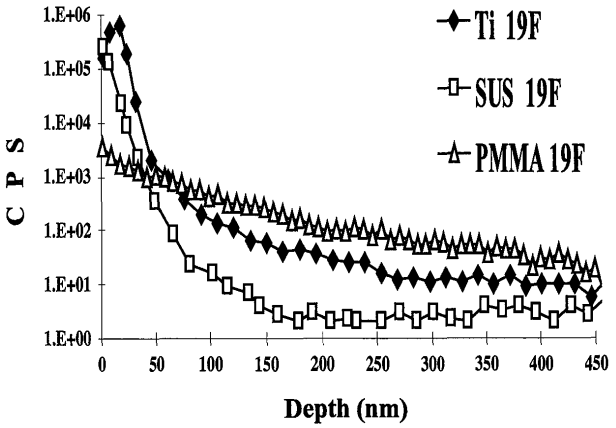

Fig. 2 Profile of F ion implantation by CF_4 gas into Ti, SUS and PMMA

Table 2. Peak count of F ion implantation (CPS)

Mean±SD

	Ti	SUS	PMMA
$Ar+F_2$	445,250 ± 165,026	196,500 ± 53,251	13.6 ± 18.0
CF_4	635,000 ± 63,535	273,250 ± 28,733	2425.0±567.9

Table 3. Depth until 10 counts of F ion implantation (nm)

Mean±SD

	Ti	SUS	PMMA
$Ar+F_2$	200.3 ± 51.1	104.5 ± 12.3	14.9 ± 17.2
CF_4	377.0 ± 151.1	173.3 ± 144.8	425.0 ± 135.7

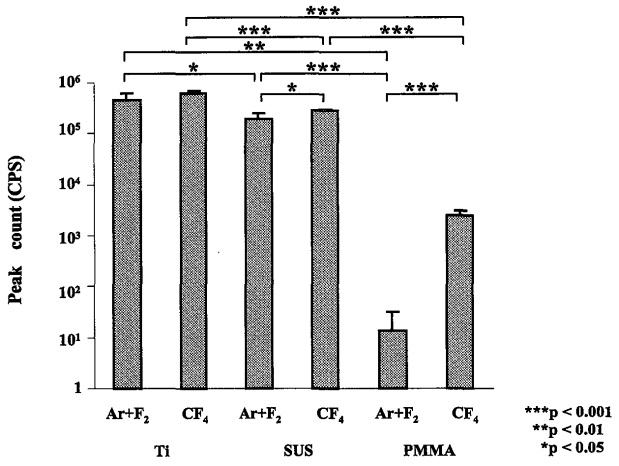

Fig. 3 Peak count of F ion implantation

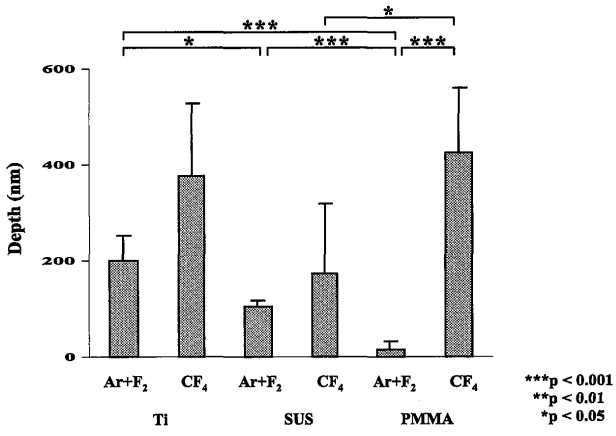

Fig. 4 Depth until 10 counts of F ion implantation

F 1s peak position was observed at 685.3 eV on the surface layer and at 685.5 eV on the second layer (Figure 5-b). Chemically shifted peaks of Cr $2p_{3/2}$ were observed in the higher binding energy region on the surface and the second layers (Figure 5-d). Chemically shifted peak of Fe $2p_{3/2}$ was observed in the higher binding energy region on the surface layer (Figure 5-f).

B. Contact angle

The contact angle of SUS is shown in Figure 6. F ion implanted group showed significantly higher contact angle than control group ($p<0.001$).

C. Surface roughness

The surface roughness of SUS is shown in Figure 7. There was no significant difference between control group and the F ion implanted group.

Surface SEM views of SUS also showed no difference between control group and the F ion implanted group (Figure 8).

D. Fluorine ion release

F ion release from the surface of F ion implanted SUS is shown in Figure 9. A small amount of F ion released until the second day. After the third day, F ion was not detected.

E. Bacterial adhesion

1) Initial adhesion

The adhesion of *S. mutans* on the surface of SUS for 4 hours incubation is shown in Figure 10. F ion implanted group showed less bacterial adhesion than control group ($p<0.001$).

2) Long-term adhesion

The results of adhesion of *S. mutans* on the surfaces of SUS for 7 and 21 days incubation are shown in Figure 11. There was no significant difference between control group and F ion implanted group in both 7 and 21 days incubation.

3) Antibacterial activity

The colony of *S. mutans* on BHI agar for antibacterial activity test of SUS is shown in Figure 12. The number of *S. mutans* (CFU/ml) in the antibacterial activity test is shown in Figure 13. F ion implanted group showed lower number of *S. mutans* than control group ($p<0.001$).

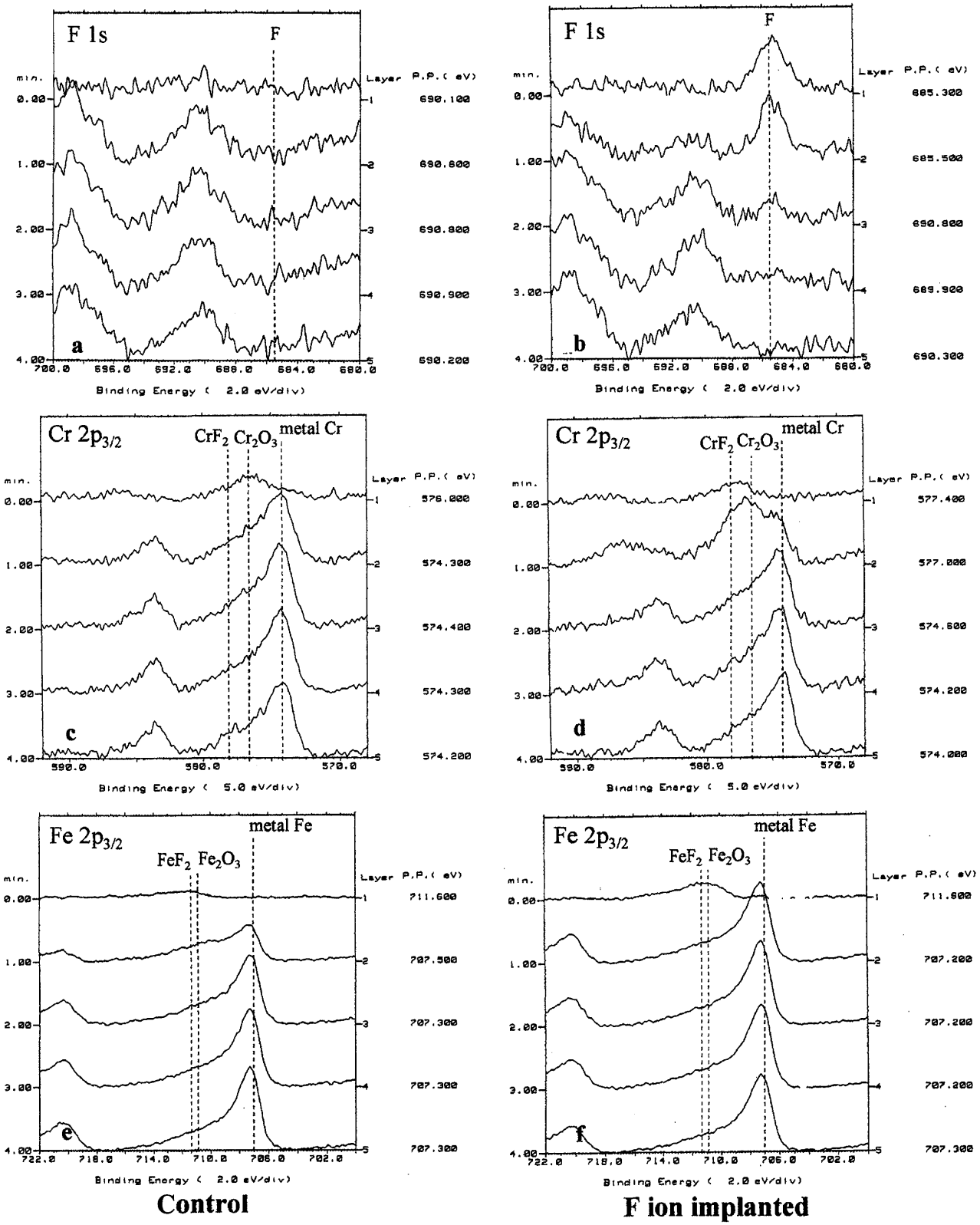

Fig. 5 F 1s, Cr $2p_{3/2}$, Fe $2p_{3/2}$ XPS spectra of SUS. Dashed lines show the peak position of F (685.5 eV), metal Cr (574.3 eV), CrF_2 (578.2 eV), Cr_2O_3 (576.6 eV), metal Fe (706.95 eV) , FeF_2 (711.4 eV) and Fe_2O_3 (710.9 eV).

Table 4. Binding energy (eV) by other works

Compound	Binding energy (eV)	Reference
F	685.5	Shimadzu Co.*)
metal Cr	574.3	D. Briggs et al. 50)
Cr_2O_3	576.6	D. Briggs et al. 50)
CrF_2	578.2	K. Hanamoto et al.49)
metal Fe	706.95	D. Briggs et al.50)
Fe_2O_3	710.9	D. Briggs et al.50)
FeF_2	711.4	D. Briggs et al.50)

*)Shimadzu Co. : XPS Spectra Sequential Peak File

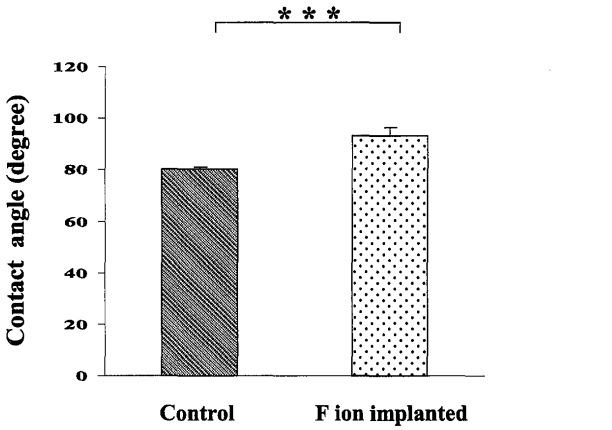

Fig. 6 Contact angle of SUS

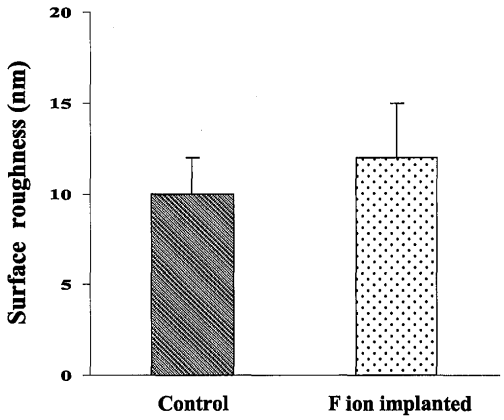

Fig. 7 Surface roughness of SUS

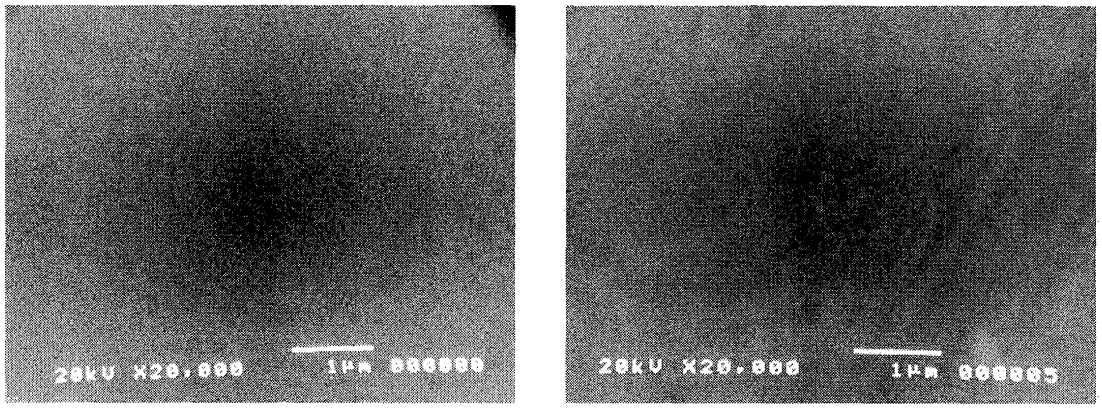

Fig. 8 Surface SEM views of SUS

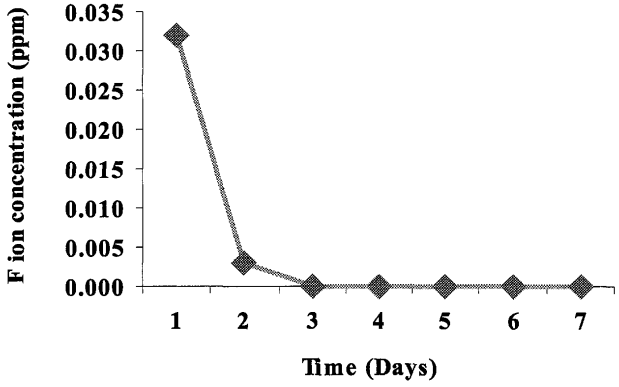

Fig. 9 F ion release

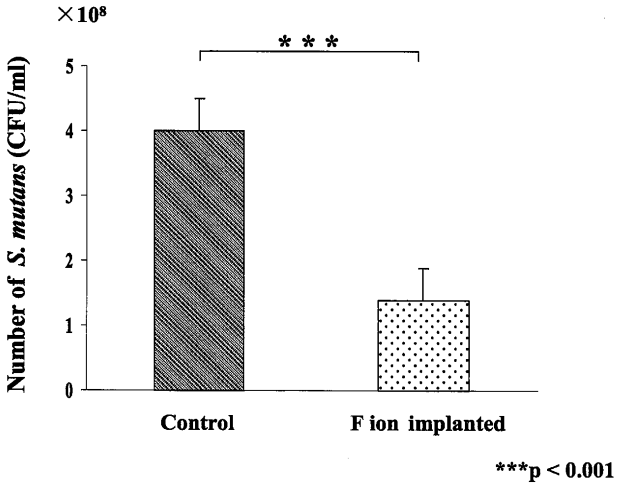

Fig. 10 Initial adhesion of *S. mutans* on the surface of SUS

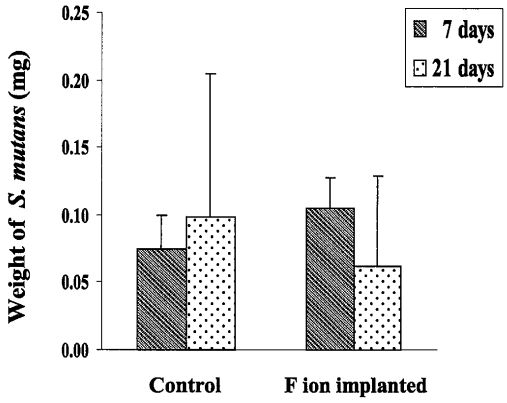

Fig. 11 Long-term adhesion of *S. mutans* on the surfaces of SUS

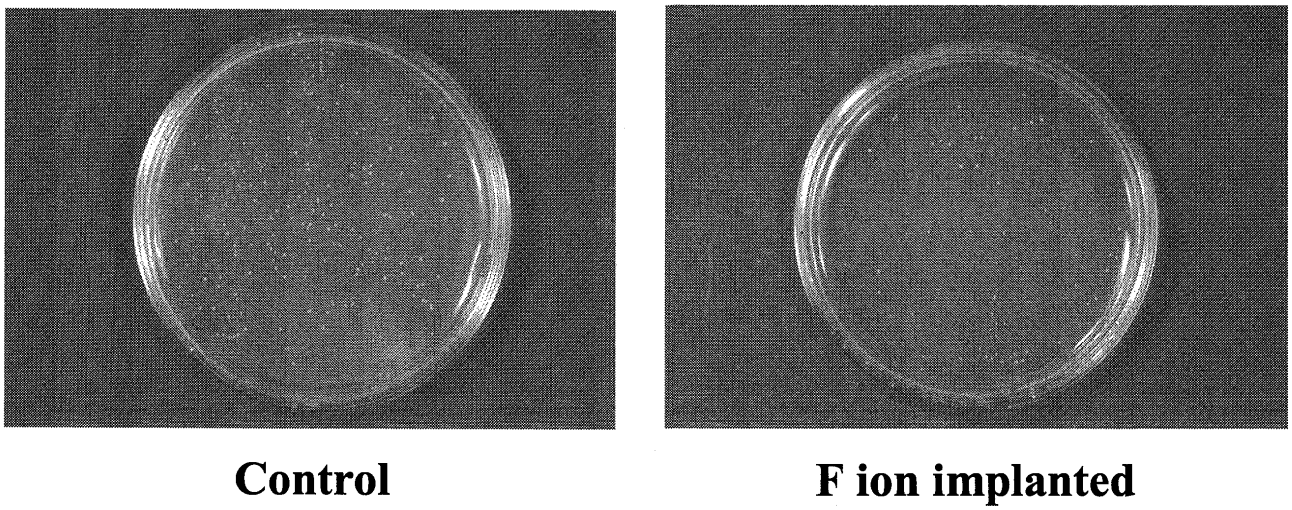

Fig. 12 Colony of *S. mutans* on BHI agar for antibacterial activity test of SUS

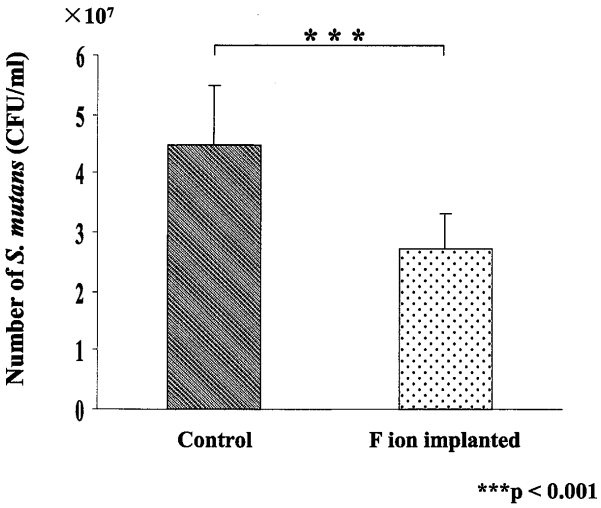

Fig. 13 Antibacterial activity of SUS

DISCUSSION

Dental appliances have complex surfaces, and plasma based ion implantation method is able to implant F ion into not only a plane surface but also a complex surface. F gas is very dangerous, therefore, CF_4, C_2F_6, SF_6 gases or mixed gas of Ar and F_2 are used for a plasma based ion implantation[35]. In this study, Ar+F_2 gas or CF_4 gas were used. F ion was implanted into Ti, SUS and PMMA.

In the present study, the peak count of F ion implanted into PMMA was significantly lower than Ti and SUS. It may be due to the insulation of PMMA. In general, the polymer interface is charged to very high voltage owing the positive charges of implanted ions without any charge compensation. The charge up problem is expected to affect the dose and implantation energy of ions[36].

The peak count of F ion implanted into Ti was the highest. But the surface of Ti plate discolored after plasma based F ion implantation. Oral prophylactic fluoride agents were reported that it could cause discoloration[37], corrosion[38-43] and increased the fracture susceptibility of Ti[44]. The corrosion resistance of Ti depends on the balance of dissolution and formation of passive film. In general, Ti and its alloys are covered with passive film (surface oxide film) consisting of low-crystallite, thin, or amorphous structures. These films are correlated to corrosion resistance[45, 46]. Strong passive films are formed on the surface of Ti, which provides high corrosion resistance under acidic environments and against various kind of chemical agents[47]. In the presence of fluoride, when the dissolved oxygen concentration is low, the reproduction of a passive film is delayed. It is suggested that the corrosion of Ti occurs because the balance shifts to the dissolution reaction of the passive film[46]. The discoloration and corrosion in the present study suggested that plasma based F ion implantation shifted the balance to dissolution of passive film.

The depth of F ion implantation by CF_4 gas into the SUS was 173.3 ± 144.8 nm in SIMS analysis and until second layer (1.0 minute Ar gas sputtering) in XPS analysis. Etching speed is different in the compounds. In Ti, etching speed by 2 keV Ar gas sputtering is about 5 nm/minute[48]. In SUS, etching speed by 0.5 keV Ar gas sputtering is about 3 Å/s[49]. Hanamoto et al[49] reported that the depth profiles of F ion implantation into 440C SUS showed 20-40 nm depend on implantation dose. These data suggest that the depth of F ion implantation into SUS may be shallow, only surface layer.

In XPS analysis, the binding energy of chromic oxide (Cr_2O_3) and chromic fluoride (CrF_2) are reported to be 576.6 eV and 578.2 eV, respectively[50](Table 4). It suggests that the shifted peak shown in the present study (Figure 5-d) was due to Cr_2O_3 and CrF_2. The binding energy of iron fluoride (FeF_2) and iron oxide (Fe_2O_3) are reported to be 711.4 eV and 710.9 eV, respectively[50]. Fe_2O_3 was detected on the surface of F ion implanted SUS. Over the second layer, the peak is close to metal Fe. Compared with F ion non-implanted control, spectra shifts did not change. This finding suggests that F does not combine with Fe.

In the present study, the contact angle of F ion implanted SUS was significantly increased. As the contact angle increases, the wettability decreases or becomes hydrophobic[51]. The contact angle can be used to calculate the surface free energy of a solid surface. Quirynen *et al.*[52] showed that a surface with a low surface free energy can delay plaque accumulation. The initial interaction between a bacterial cell and the materials is influenced by the physico-chemical properties of the material surface contaminated by salivary or crevicular fluid components. The first physico-chemical factor of the adhesion process is the surface free energy. It is known that organic polymers are generally hydrophobic with a lower surface energy as compared with inorganic materials such as glass and metals are hydrophilic with a higher surface energy. Depending on the hydrophobicity of both bacteria and material surfaces, bacteria adheres differently to materials with different hydrophobicities[32, 53, 54]. Dankert *et al.*[55] showed that a hydrophobic bacterium adheres 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. In accordance to this hypothesis, the finding of this present study that initial adhesion of *S. mutans* on the surface of F ion implanted SUS significantly decreased was suggested due to significant increase of contact angle.

Surface roughness influences bacterial adhesion. In general, it is believed that smooth surface has a lower potential for plaque formation than rough surface[56]. The cause for this phenomenon may include that rough surface has a greater surface area and the depressions in the roughened surface provide favorable sites for colonization. In this present study, F ion implantation had no effect to surface roughness of SUS.

Verbeeck *et al.*[57] reported that the fluoride release from glass-ionomer cement or composite resin occurred at two different process. The first process was characterized by an initial burst of fluoride release, after which the fluoride release was markedly reduced and continued for a long period of time. In the present study, a small amount of F ion released from the surface of F ion implanted SUS within 24 hours and an extremely small amount of F ion was detected until two days, but was not detected after three days. This finding suggested that the small amount of F ion released not from the inside but from the F ion contaminated surface.

Initial (4 hours) and long-term (7 days and 21 days) adhesion of *S. mutans* on the surface of SUS was evaluated.

The initial adhesion of the F ion implanted SUS significantly decreased compared with F ion non-implanted control. This finding may be due to the increase of contact angle as described as above, and antibacterial activity as described as follows. In the long-term adhesion, there was no significant difference between control group and F ion implanted group. This finding suggests that the effects of contact angle and antibacterial activity are only on the surface of F ion implanted group and no effect on the adhered bacterial film. In the present study, the F ion implanted SUS showed the antibacterial activity. Some surface modification with dry process such as ion implantation was reported as useful for controlling the initial adhesion of oral bacteria and the F^+ implanted to Ti surface exhibited antibacterial activity effectively against both *P. gingivalis* and *A. actinomycetemc omitans*[58]. Li *et al.*[59] reported that the cell attachment on the PMMA surface could be controlled by F^+ ion implantation. It has been reported that several fluoride salts with polyvalent cations such as Cu^{2+}, Sn^{2+} and Al^{3+} exhibit a direct antibacterial effect. There are two possible explanations for antibacterial mechanism of the F^+ implanted materials. One is the action of the F ions and the other is the action of metal fluoride complexes. F ion released from fluoride can affect bacterial metabolism as an enzyme inhibitor, for example for the glycolytic enzyme enolase. The metal fluoride complexes are responsible for fluoride inhibition of proton-translocating F-ATPase and are thought to act by mimicking phosphate to form complexes with ADP at reaction centers of the enzyme[30, 31]. ATPase plays an important role in the maintenance of the intracellular pH by pumping out protons; inhibition of this enzyme disrupts the bacterial metabolism and the acid uric capability of *S. mutans*[60-62]. Considering the results from XPS, spectra of F ion implanted SUS showed CrF_2. This metal fluoride complexes might be responsible for antibacterial activity.

CONCLUSIONS

The purposes of the present study were to evaluate the profile and spectra of plasma based F ion implantation into the surface of dental materials and to evaluate the effects of F ion implantation on the contact angle, surface roughness, F ion release and the bacterial adhesion.

F ion was implanted over the surface and subsurface layer of Ti, SUS and PMMA. For plasma based F ion implantation, CF_4 gas was more suitable than $Ar+F_2$ gas. XPS analysis of F ion implanted SUS showed the presence of CrF_2 on the surface.

The F ion implantation into SUS significantly increased contact angle, significantly decreased 4 hours *S. mutans* adhesion and significantly increased anti *S. mutans* activity of the surface.

The decrease of *S. mutans* adhesion and increase of anti *S. mutans* activity might be from the action of F ion and metal fluoride complexes such as CrF_2. The plasma based F ion implantation into the dental materials could inhibit bacterial adhesion on the surface of the dental materials.

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