Dental Materials Journal 2010; 29(1): 53–58

Corrosion behavior of ion implanted nickel-titanium orthodontic wire in fluoride mouth rinse solutions

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This study investigated the corrosion properties of ion implanted nickel-titanium wire (Neo Sentalloy Ionguard) in artificial saliva and fluoride mouth rinse solutions (Butler F Mouthrinse, Ora-Bliss). Non ion implanted nickel-titanium wire (Neo Sentalloy) was used as control. The anodic corrosion behavior was examined by potentiodynamic polarization measurement. The surfaces of the specimens were examined with SEM. The elemental depth profiles were characterized by XPS. Neo Sentalloy Ionguard in artificial saliva and Butler F Mouthrinse (500 ppm) had a lower current density than Neo Sentalloy. In addition, breakdown potential of Neo Sentalloy Ionguard in Ora-Bliss (900 ppm) was much higher than that of Neo Sentalloy although both wires had similar corrosion potential in Ora-Bliss (450 and 900 ppm). The XPS results for Neo Sentalloy Ionguard suggested that the layers consisted of TiO_2 and TiN were present on the surface and the layers may improve the corrosion properties.

Keywords: Ni-Ti wire, Corrosion, Plasma immersion ion implantation

Received Aug 10, 2009: Accepted Oct 5, 2009

INTRODUCTION

Nickel-titanium wires, which have a near-equiatomic composition, were introduced to orthodontic clinical use by Andreasen and colleagues in the early 1970s[1]. They have been highly popular because they have a much lower elastic modulus and wider elastic range than other orthodontic wires such as those composed of beta-titanium, stainless steel, and cobalt-chromium-nickel[2,3].

For patients with orthodontic fixed appliances, mouth rinsing with fluoride-containing products is an effective method for the prevention of caries because such appliances have complicated morphologies[4]. However, reduced corrosion resistance of pure titanium and titanium alloys in fluoride-containing environments that attack the protective surface oxide has been reported[5-7]. The corrosion resistance of pure titanium and titanium alloys largely depends on the fluoride concentration and the pH value[8]. Although fluoride solutions should be important for preventing dental caries in orthodontic patients, they may promote the corrosion of titanium alloy orthodontic wires.

Recently, a plasma immersion ion implantation (PIII) technique has become quite common in the surface-coating industry to improve the mechanical properties and corrosion resistance of titanium alloys[9-11]. About 10 years ago, ion implanted nickel-titanium wire (Neo Sentally Ionguard, GAC International, Islandia, NY, USA) and beta-titanium wire (Low Friction TMA, Ormco, Glendora, CA, USA) were introduced. Jia *et al.*[12] reported that nitrogen-implanted nickel-titanium wires released significantly fewer nickel ions in artificial saliva than conventional nickel-titanium wires. However, there has been no study on the corrosion properties of ion implanted nickel-titanium wire in a fluorine-containing environment, even though previous reports have revealed[13-15] that the corrosion resistance of orthodontic titanium and nickel-titanium alloy was decreased in such an environment.

The purposes of this study were to investigate the corrosion properties of ion implanted nickel-titanium orthodontic wire in fluoride mouth rinse solutions. The electrochemical properties were determined by potentiodynamic polarization measurements in artificial saliva and mouth rinse solutions with various fluoride concentrations and pH values. A surface analysis was also performed with X-ray photoelectron spectroscopy (XPS) to evaluate the passive film on the top surface of as-received wire.

MATERIALS AND METHODS

Materials

The orthodontic wires used in the present study were Neo Sentally Ionguard (GAC International, Islandia, NY, USA) and Neo Sentally (GAC International). Both wires had cross-section dimensions of 0.016 × 0.022 inches and had the same compositions, except that nitrogen ion was implanted on the surface of Neo Sentalloy Ionguard during the manufacturing process.

Potentiodynamic polarization measurement

The anodic corrosion behavior of as-received wires was examined by potentiodynamic polarization measurement in artificial saliva and mouth rinse solutions with various fluoride concentrations and pH values at 37°C (n=3 wire types/test solutions). Table 1 summarizes the test solutions used in the present study. The two types of fluoride mouth rinse solutions

Table 1 Summary of test solutions used in this study

Tests solutions	Manufacturer	Composition	F-(ppm)	pH
Artificial saliva	–	NaCl, 0.4 g; KCl, 0.4 g; $CaCl_2 \cdot 2H_2O$, 0.795 g; $NaH_2PO_4 \cdot 2H_2O$, 0.78 g; $Na_2S \cdot 9H_2O$, 0.005 g; NH_2CONH_2, 1.0 g; distilled water, 1000 ml	–	5.9
Butler F Mouthrinse 0.1%	Sunstar Inc.	NaF (small amouts of $NaH_2(C_3H_5O(COO)_3)$, $C_{21}H_{38}NCl$, and $C_3H_8O_2$, $C_6H_8O_7$)	500	6.0
Ora-Bliss	Showa Yakuhin Kako Co.,Ltd.	NaF	450	5.1
			900	5.1

used in this study were Butler F Mouthrinse 0.1% (Sunster Inc., Osaka, Japan) and Ora-Bliss (Showa Yakuhin Kako Co., Ltd., Tokyo, Japan). The fluorine concentration of the Butler F Mouthrinse 0.1% was 500 ppm and the Ora-Bliss was made with two different concentrations (450 ppm and 900 ppm). The pH values of these fluoride mouth rinse solutions at 37ºC were 6.0 for Butler F Mouthrinse 0.1% and 5.1 for both concentrations of Ora-Bliss. The solutions were deaerated by bubbling with ultra-high-purity argon gas at the rate of 150 cm^3/min for at least 60 min before the sample was introduced to the three-electrode cells and then bubbling at a lower rate was continued throughout the measurement. A platinum wire and Ag/AgCl electrode were used as a counter and a reference electrode, respectively. At 60 min after specimen immersion, the polarization measurements were carried out using a potentiostat (HZ-3000, Hokuto Denko , Tokyo, Japan) starting from the free corrosion potential at a scan rate of 10 mV/min.

Scanning electron microscope (SEM) observation

One as-received and one representative specimen that were used for potentiodynamic polarization measurements of each wire type were examined with a scanning electron microscope (SSX-550, Shimadzu, Kyoto, Japan). All specimens were sputter-coated with gold and examined with a SEM operating at 15 kV.

Surface analysis (Depth profile)

The elemental depth profiles of as-received wires were characterized by X-ray photoelectron spectroscopy (XPS; ESCA-850; Shimadzu, Kyoto, Japan), with Al Kα radiation at 7 kV and 30 mA, under a pressure of 1×10^{-6} Pa. An argon ion sputtering rate of 0.1 nm/sec was used to determine the chemical compositions of the surface and subsurface layers. Each test specimen consisted of several segments, approximately 5 mm in length, placed side by side to compare the results without and with argon ion sputtering maximum 1,800 seconds on the surface. A take-off angle of 90° was used for all specimens. The surface composition (at.%) was calculated from the relative XPS peak intensity using computer software (CasaXPS, Casa Software Co., Ltd.) that considered variations in atomic sensitivity.

RESULTS

Figs. 1 and 2 show representative potentiodynamic polarization curves for the specimens in artificial saliva and each mouth rinse solution. Neo Sentalloy Ionguard in artificial saliva had a lower current density than Neo Sentalloy over the entire potential range (Fig. 1). Also, Neo Sentalloy Ionguard in Butler F Mouthrinse 0.1% showed a lower current density than Neo Sentalloy over the entire potential range (Fig. 2). Both wires (Neo Sentalloy Ionguard and Neo Sentalloy) in Ora-Bliss 450 ppm showed similar corrosion properties, and the current density was higher than those in artificial saliva and Butler F Mouthrinse 0.1%. On the other hand, corrosion with highly localized pitting was seen in Ora-Bliss 900 ppm for Neo Sentalloy, and the breakdown potential of Neo Sentally was much lower than that of Neo Sentalloy Ionguard.

Representative SEM photomicrographs of Neo Sentalloy Ionguard and Neo Sentalloy, both as-received and after potentiodynamic polarization measurements, are shown in Fig. 3. Localized corrosion was not observed for both types of wires in artificial saliva, Butler F Mouthrinse 0.1% and Ora-Bliss 450 ppm (Fig.3c, d, e, f, g, h). On the other hand, many visible cracks and grooves, propagated deep into the alloy during potentiodynamic polarization measurement in Ora-Bliss 900 ppm, were observed for Neo Sentalloy (Fig.3i). Small pits were seen in Ora-Bliss 900 ppm for Neo Sentalloy Ionguard (Fig.3j).

Fig. 4 shows Ti 2p, Ni $2p_{3/2}$ and N 1s spectra obtained from the Neo Sentalloy surface. Spectra without argon ion sputtering (top surface) are shown at the top, and those with argon ion etching (80 and 300 seconds) are shown at the middle and bottom. Strong Ti 2p peaks at about 459 eV and about 465 eV at the top surface were assigned to TiO_2. The peaks at about 455 eV and 461 eV corresponding to metallic Ti under an oxide film were clearly seen after argon ion sputtering. Similarly, the major Ni $2p_{3/2}$ peak at about 853 eV was clearly observed after argon ion sputtering, and this peak was assigned to metallic nickel under the surface film. For N 1s, a small peak at about 401 eV was observed at the top surface, and this probably corresponded to the organic substance of some

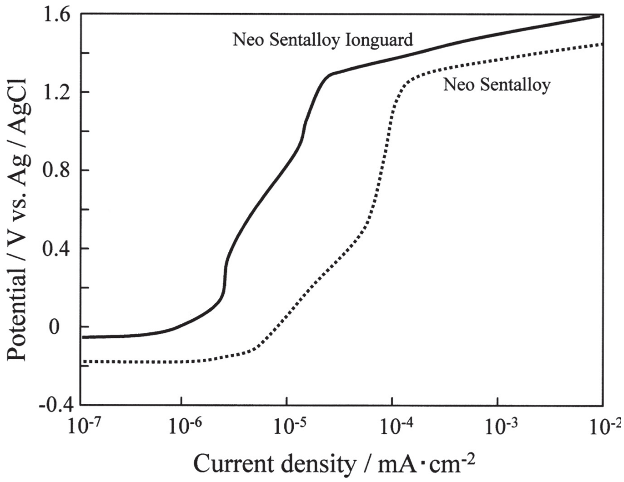

Fig. 1 Potential/current density curves of Neo Sentalloy and Neo Sentalloy Ionguard in artificial saliva.

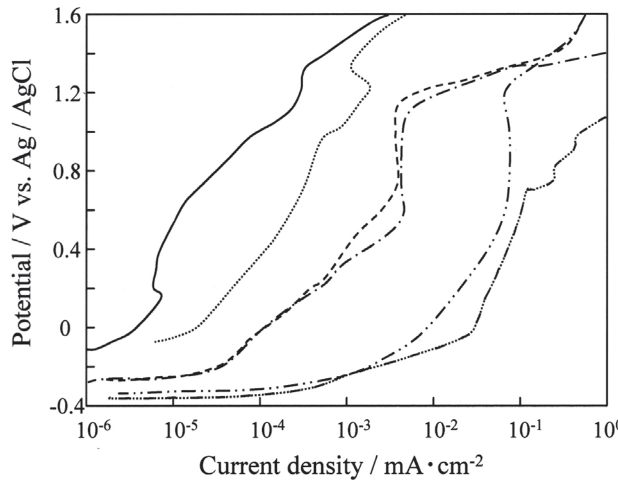

Fig. 2 Potential/current density curves of Neo Sentalloy and Neo Sentalloy Ionguard.

———: Neo Sentalloy Ionguard in Butler F Mouthrinse 0.1%
···········: Neo Sentalloy in Butler F Mouthrinse 0.1%
– – – –: Neo Sentalloy Ionguard in Ora-Bliss 450 ppm
–·–·–: Neo Sentalloy in Ora-Bliss 450 ppm
–··–··–: Neo Sentalloy Ionguard in Ora-Bliss 900 ppm
–···–···–: Neo Sentalloy in Ora-Bliss 900 ppm

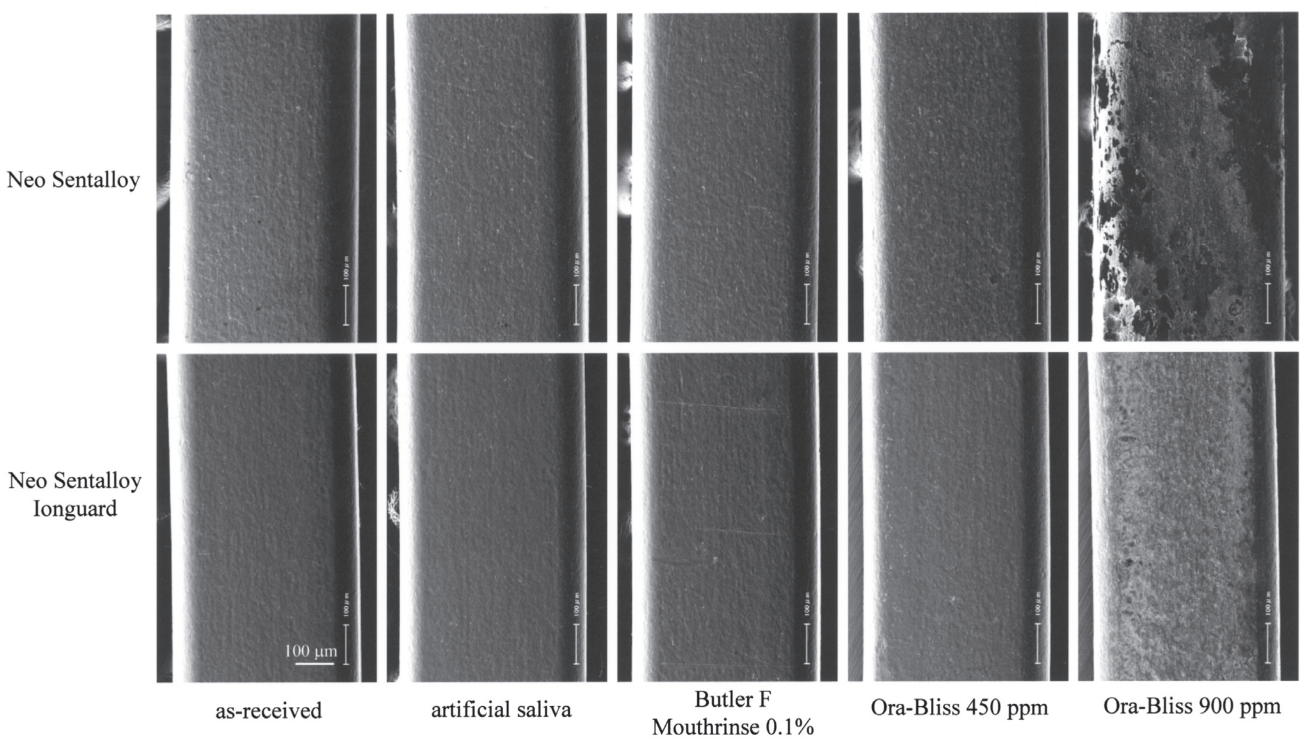

Fig. 3 SEM photomicrographs of Neo Sentalloy and Neo Sentally Ionguard before and after anodic polarization measurement in artificial saliva, Butler F Mouthrinse 0.1%, Ora-Bliss 450ppm and Ora-Bliss 900 ppm.

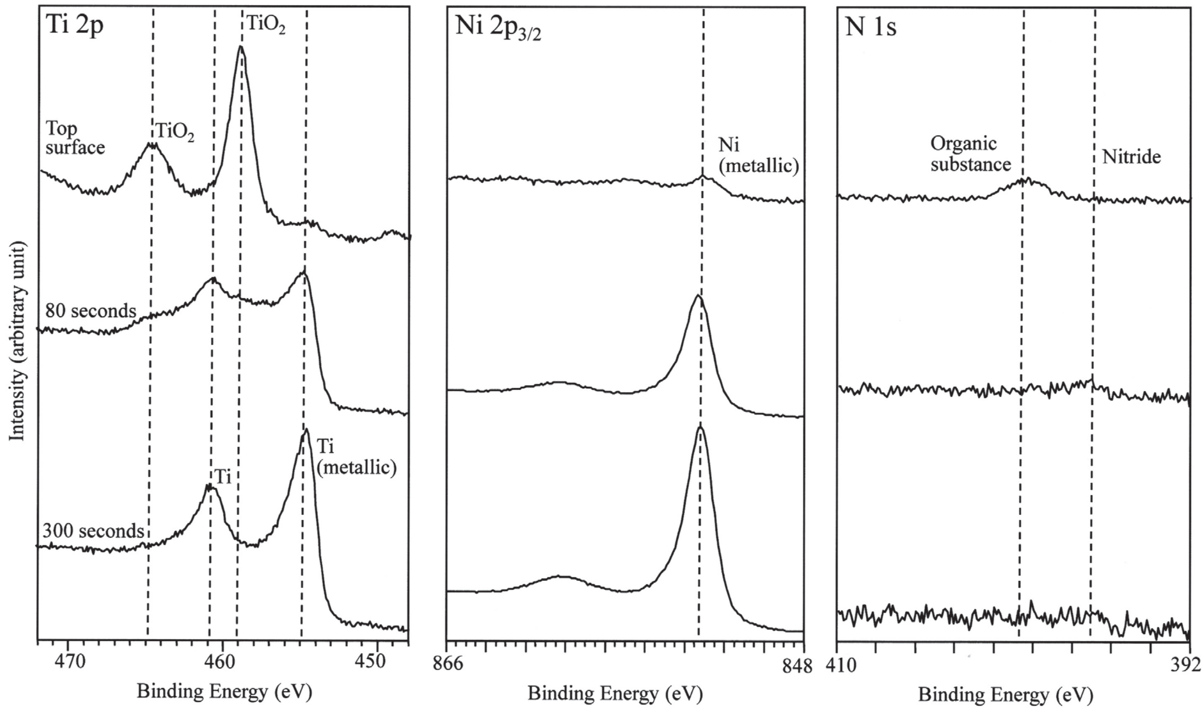

Fig. 4 XPS spectra without and with argon ion sputtering (80 and 300 seconds) on the surface of Neo Sentalloy.

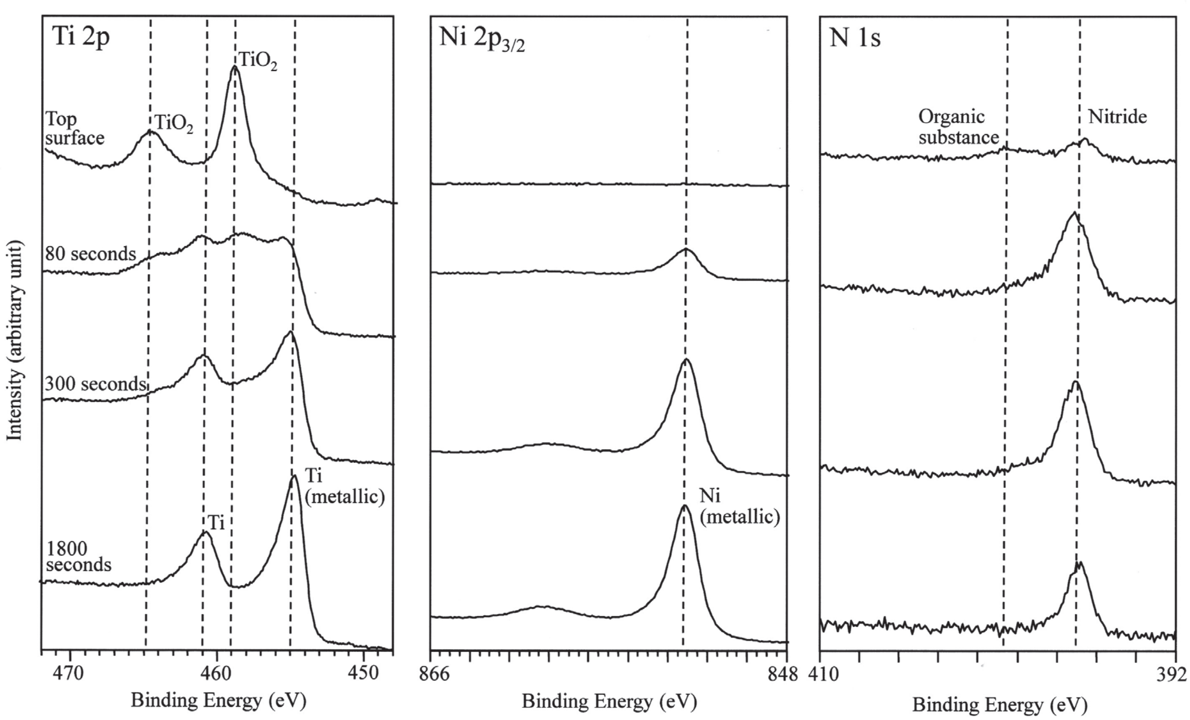

Fig. 5 XPS spectra without and with argon ion sputtering (80, 300 and 1,800 seconds) on the surface of Neo Sentalloy Ionguard.

contaminant. Fig. 5 shows Ti 2p, Ni $2p_{3/2}$ and N 1s spectra obtained from the Neo Sentalloy Iomguard surface. For Ti 2p spectra, the peaks at about 459 eV and 465 eV at the top surface were assigned to TiO_2. Peaks corresponding to metallic titanium (455 eV and 461 eV) and metallic nickel (853 eV) were clearly observed after argon ion sputtering. For N 1s spectra, a strong peak at about 397 eV corresponding to Nitride was clearly observed after argon ion sputtering, and this peak was recognized even after 1,800 seconds of argon ion sputtering.

DISCUSSION

Since biocompatibility is closely related to corrosion properties, there has been growing interest in the corrosion phenomena of orthodontic alloys in the oral environment[16-18)]. Recently, the corrosion behavior of nickel-titanium orthodontic wire has been widely studied with regard to the effects of a fluorine-containing environment[13-15)], various temperatures[19)], bending stress[20)] and galvanic corrosion[4,21,22)]. It is well known that nickel-titanium orthodontic wire has high corrosion resistance due to a protective TiO_2 film formed on the top surface[23,24)]. However, the corrosion resistance of nickel-titanium orthodontic wire should be improved for safer clinical use because nickel is known to trigger more allergic reactions than other metals such as cobalt and chromium[25,26)]. The PIII technique, which incorporates carbon, oxygen or nitrogen into titanium alloys, has been commonly used for the surface modification of biomaterials to improve their mechanical and corrosion properties[9-11)]. PIII with nitrogen formed a TiN layer on the surface, which produced higher corrosion resistance and mechanical properties[10,11)]. Moreover, previous reports have shown that the surface layers newly formed by PIII do not affect the bulk transformation characteristics of nickel-titanium alloys, such as the shape memory effect and superelastic property[10,11)]. In the surface analysis in the present study, Ti 2p for Neo Sentally (Fig. 4) showed the presence of TiO_2 at the top surface along with an organic substance of some contaminant, which agreed with previous reports regarding nickel-titanium alloy[11,23)]. On the other hand, N1s spectra for Neo Sentalloy Ionguard showed a strong peak for Nitride after ion sputtering in addition to peaks for titanium oxide on the top surface (Fig. 5), suggesting that the layers consisted of TiO_2 and TiN[27)] formed on the surface of Neo Sentalloy Ionguard probably act as a barrier to prevent released metal ions and improve repassivation in the high potential region. Another possible reason why Neo Sentalloy Ionguard showed higher corrosion resistance was the small amount of Ni (metallic) under the surface oxide film.

The use of fluoride-containing products, such as fluoride-containing toothpastes, gels, mouthwashes, APF solutions and composite resins for bonding brackets, has become common in clinical orthodontics to achieve good oral hygiene care[28,29)]. The fluoride level in the oral environment varies according to the prophylactic treatment used. Although titanium alloys show excellent corrosion resistance due to the highly protective TiO_2 oxide film on the top surface[23)], numerous reports have shown that the corrosion resistance of titanium alloys decreased in the presence of fluoride ions[13-15)]. In an acidic environment, fluoride ions form hydrofluoric acid (HF), and a HF concentration of over 30 ppm resulted in dissolution of the passive film of titanium alloys[6)]. The present study demonstrated that the corrosion potential of Neo Sentalloy Ionguard in both concentrations of Ora-Bliss with slightly acidic pH (5.1) was similar to that of Neo Sentalloy, and the current densities obtained with both wires were much higher than those in artificial saliva and Butler F Mouthrinse 0.1% with relatively higher pH. However, the breakdown potential for Neo Sentalloy Ionguard in Ora-Bliss (900 ppm) was much higher than that for Neo Sentalloy. Therefore, it seems appropriate to remark that, although TiO_2 layer formed on the top surface of Neo Sentalloy Ionguard may be dissolved by HF, which was produced by increasing the fluoride concentration or lowering pH value, TiN layer probably act to maintain low susceptibility to localized corrosion.

CONCLUSIONS

Under the conditions in this study, the following conclusions can be drawn:

1. The corrosion properties of nickel-titanium orthodontic wire are influenced by nitrogen ion implantation.
2. Neo Sentalloy Ionguard (nitrogen-implanted nickel-titanium wire) showed higher corrosion resistance in artificial saliva and neutral fluoride mouth rinse solution than Neo Sentalloy.
3. Neo Sentalloy Ionguard showed low susceptibility to localized corrosion.

ACKNOWLEDGMENTS

This research was supported in part by a Grant-in-Aid Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan (No. 19592363).

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