Corrosion resistance and mechanical properties of titanium nitride plating on orthodontic wires

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Titanium nitride (TiN) coating by ion plating has properties such as high hardness, wear resistance, corrosion resistance, and surface lubricity, therefore TiN coating is often used in various dental appliances and materials. In this study, we evaluated the corrosion behaviors and mechanical properties of TiN coated stainless steel (SS) and nickel titanium (Ni-Ti) orthodontic wires prepared by ion plating. TiN coating by ion plating improves the corrosion resistance of orthodontic wires. The corrosion pitting of the TiN coated wire surface become small. The tensile strength and stiffness of SS wire were increased after TiN coating. In contrast, its elastic force, which is a property for Ni-Ti wire, was decreased. In addition, TiN coating provided small friction forces. The low level of friction may increase tooth movement efficiently. Therefore, TiN coated SS wire could be useful for orthodontics treatment.

Keywords: Titanium nitride, Ion plating, Orthodontic wire

INTRODUCTION

Plating has become an important method to protect materials from wear and corrosion. Physical vapor deposition (PVD) methods such as sputtering, vacuum deposition, and ion plating are well established for the development of metal coatings. PVD-type ion plating is a surface modification technique that can be used to fabricate thin surface layers on substrates. Among the various techniques and materials suitable for producing such a coating on metal, TiN ion plating was used in this study. The advantages of this coating are that it can be coated at a low temperature and forms a reaction layer. Further, Ti atoms are known to form a passivity film on Ti surfaces when combined with oxygen in various solutions1,2. TiN forms a passivity film of TiO2 on the surface in various solutions. Especially, it has been reported that titanium nitride (TiN) layers fabricated by ion plating demonstrate favorable corrosion resistance3, wear resistance4, hardness5, and friction6.

It is well known that SS is prone to pitting and crevice corrosion in solutions containing chloride ions6. Paschoal et al.7 showed that TiN coatings on SS prepared by PVD brought about improved corrosion resistance indicated by better passivation. Liu et al.9 showed that TiN coating improved corrosion resistance during anodic polarization tests, however, the elution of metal ions from Ni-Ti plate increased after TiN coating. They suggested that the causes of this phenomenon may have been the columnar microstructure, micro-particles, and pinholes in the coatings. In contrast, Zhang et al.3 showed that TiN plating significantly suppressed the release of Ni ions from nitinol atrial septal defect (ASD) occluders both in vivo and in vitro. Endo et al.9 demonstrated that the breakdown potential of TiN coated Ni-Ti plate decreased in 0.9% NaCl solution during anodic polarization. Thus, various results have been reported for the corrosion resistance of TiN-platings. The reasons for these discrepancies might be differences in the thickness of the TiN layer, the surface properties of the TiN layer, and the adhesion between the substrate and TiN layer in each experiment. Further studies are needed to clarify this point. Because orthodontic wire is placed into bracket slots, the thickness of the coating is important. Navinsek et al.10 reported that the typical coating thickness obtained by PVD processes is thinner than that by electroplating and electroless plating. Thus, the change in the dimensions of the TiN coated wire was small, because the TiN film deposited by the ion plating was very thin. Therefore, TiN coating by ion plating may be useful as a coating on the orthodontic wire.

Since TiN coating has appropriate properties such as high hardness, wear resistance corrosion resistance, and surface lubricity, therefore TiN coating is often used in various dental appliances and materials7,8,9. However, there are few reports that the properties of TiN coated orthodontic appliances. Some evaluation of coating on brackets has been carried out, and it has been reported that the friction force of TiN coating on brackets did not change, while other paper reported that the friction force was reduced when the brackets was coated by diamond-like carbon (DLC)11,12. The stainless steel (SS) and nickel titanium (Ni-Ti) wire has been used most...
widely wire in orthodontic treatment. The hardness, corrosion resistance, wear resistance, and low friction between wire and bracket are important factors for orthodontic treatment in orthodontic wires. However, the property of TiN coated orthodontic wire has not been reported.

In this study, we performed the ion plating of TiN coatings onto orthodontic wires, namely SS and Ni-Ti wires, and evaluated the change in corrosion resistance by analysis of released ions, electrochemical methods, and surface observation by microscopy. The mechanical properties were analyzed by tensile test, 3-point bending test, and friction test.

**MATERIALS AND METHODS**

**TiN ion plating**

SS and Ni-Ti wires (0.016×0.022 inch) were used as the specimens in these studies (American Orthodontics, Sheboygan, WI, USA). TiN coatings were fabricated on the wire substrates by the hollow cathode discharge method. Each wire was cut to a length of 180 mm and then wiped with ethanol. The wires were first placed in an ion-plating apparatus (HCD ion plating device X-27, Tigold, Chiba, Japan) under a pressure of 1.33×10⁻² Pa. TiN ion plating was performed under argon (Ar) gas/nitrogen (N₂) gas mixture, and −20 V bias voltage. Ar gas partial pressure was 1.49 Pa and N₂ gas partial pressure was 1.69 Pa. The substrate temperature was maintained at approximately 220°C for 7 min using a heat source. Ar plasma and N₂ plasma were used for the TiN layer deposition and a mixture of Ar and N₂ was used for the TiN layer. The coating process was performed by holding both side of the wire and rotating it. After the TiN coating had completely covered the original wires, except for their ends, the wires were slowly cooled for 1 h in vacuum. The TiN thickness was measured the layer thickness on the stainless steel board which was put near wires.

The observation of TiN layer surface

To determine the thickness of the TiN coating, TiN coated wires were embedded in phenol resin (PolyFast, Struers, Sarasota, FL, USA) and then were polished using a series of silicon carbide (80#–1500#) and diamond paste (6 and 1 µm) so as to provide a cross section of the coated surface of the wire. The polished cross sections of the wire were secured conductivity by osmium coating and observed using scanning electron microscope (SEM, VE-7800, Keyence, Osaka, Japan) at an accelerating voltage of 15 kV. Four replicates of each wire were tested. In addition, the surface roughness (Ra) was measured using atomic force microscopy (AFM 5100N, Hitachi, Tokyo, Japan). The scanning area was 20×20 µm².

**Electrochemical corrosion**

Electrochemical corrosion tests were conducted with reference to the methods described below¹⁵). Each wire was covered with a masking agent (Sunecon, Taiyo Chemicals & Engineering, Tokyo, Japan) except for the connecting part and the measuring part, which were 10 mm in length. The measuring part was immersed into the electrolytic solution. Platinum (Pt) and silver-silver chloride (Ag/AgCl) electrodes were used as the counter and reference electrodes, respectively. NaCl solution was deaerated with N₂ gas at 40°C for 1 h. Anodic polarization tests were carried out in 0.9% NaCl solution at 37°C with a potentiostat (HZ-5000, Hokuto Denko, Tokyo, Japan) started from the −0.4 to 1.0 or 2.0 V at a scan rate of 0.6 mVs⁻¹, and the polarization curve of each wire was recorded to measure the breakdown potential. The potential at which there was a sharp increase in anodic current density in the curve was taken as the breakdown potential¹⁶). Four replicates of each wire were tested. We observed the surface of the TiN coated wire at the slightly higher potential than the breakdown potential of the non-coated wires (SS wire: 0.5 V, Ni-Ti wire: 1.4 V) and at the end of anodic polarization tests (SS wire: 1.0 V, Ni-Ti wire: 2.0 V). The surface of the SS and Ni-Ti wire specimens was observed using an optical microscope (BX-51, Olympus, Tokyo, Japan).

**Tensile test**

Tensile tests were accomplished using a universal testing machine (Micro Tester Model 5948, Instron, Norwood, MA, USA) with a 2,000 N load cell at a crosshead speed of 1 mm/min. The span of the wire between grips was standardized at 20 mm. SS wires were stretched until break, at a crosshead speed of 1 mm/min. Four replicates of each SS wire were tested. The tensile strength, 0.2% proof stress, modulus of elasticity, and breaking elongation were determined using the stress-strain curve obtained.

**Three-point bending test**

The flexural properties of the wires were estimated with the three-point bending test using a creep meter (Re2-33005S, Yamaden, Tokyo, Japan). The span length between fulcums was 14 mm. A crosshead placed on the center of the specimen was engaged to move downward at a rate of 6 mm/min, causing the specimen to bend to a final displacement of 3.1 mm under the applied load, and unloaded until the initial position. The force and displacement were recorded and the force-displacement curves were plotted from the obtained data. The flexural rigidity and 0.1 mm offset bending strength of SS wires were evaluated. The Ni-Ti wires were evaluated from their unloading bending forces at deflections of 3.0, 2.0, 1.0, and 0.5 mm. Six replicates of each wire were tested.

**Friction test**

This test was conducted with reference to the methods as below¹⁷). Friction forces of the wires were estimated with the friction test using a creep meter (Re2-33005S, Yamaden, with a 20 N load cell. Two types of brackets were used: metal brackets (Metal bracket; Dentsply, Tokyo, Japan) and plastic brackets (Crystabrace7, Dentsply). Both metal and plastic upper right central
incisor brackets (0.018×0.025 inch slot size) were used. Each bracket was bonded with a cyanoacrylate adhesive (Aron Alpha, Toagosei, Tokyo, Japan) to a wooden block which bonded on the creep meter (Fig. 1A). Each wire, 50 mm in length, was ligated to the bracket with elastomeric modules (Mini Stix ligature Ties, TP Orthodontics, Indiana, USA). The upper end of the wire was fixed in a grip that was attached to the load cell, and the lower end of the wire was free. The span of the wire between grip and bracket center was standardized at 20 mm (Fig. 1B). The upper end of the wire was pulled upward 5.0 mm at a speed of 0.1 mm/s for friction force measurements. Each bracket/wire combination was submitted to mechanical tensile test at angulations of 0 and 10 degrees (Figs. 1C, D) and six replicates of each material were tested in both conditions. The friction force values were indicated by averaged from 0.5 s after the start of the measurement until end of the measurement.

**Statistics**

Data are shown as mean±standard deviations. Data comparison was carried out using the Mann-Whitney U test, with the value of significance set at p<0.05.

**RESULTS**

**Uniform coating of the TiN layer to the wire surface**

SEM from a cross-section of the TiN-coated SS and Ni-Ti wires clearly showed the TiN coating to have a thickness of 0.579±0.007 and 0.582±0.011 µm, respectively (data not shown). The surface roughness of TiN layer was also analyzed using AFM. Ra of the non-coated and the TiN coated SS wire was 0.023 and 0.046 µm, and that of the non-coated and the TiN coated Ni-Ti wire was 0.001 and 0.001 µm, respectively (Fig. 2).

**Increase in the corrosion resistance of orthodontic wire with TiN ion plating**

The representative polarization curves for both the TiN coated and the non-coated wires are shown in Fig. 3. The breakdown potential of the non-coated and the TiN coated SS wire was 0.46±0.05 and 0.61±0.04 V (p<0.05), and that of the non-coated and the TiN coated Ni-Ti wire was 1.20±0.03 V and more than 2.0 V, respectively. The current densities at the passive region of both TiN coated wires were lower than those of both non-coated wires, respective. The surface of the SS and Ni-Ti wires was observed by optical microscopy at the slightly higher potential than the breakdown potential of the non-coated wire (SS wire: 0.5 V, Ni-Ti wire: 1.4 V). The non-coated SS and Ni-Ti wires were observed some pitting corrosions. No large pitting corrosion was observed on the surface of the TiN coated wires (Fig. 4A). At the end of anodic polarization tests (SS wire: 1.0 V, Ni-Ti wire: 2.0 V), the non-coated SS and Ni-Ti wires showed large pitting corrosion. In contrast, no such large pitting corrosion was observed on the TiN coated wires (Fig. 4B).

**Increase in the tensile strength and proof stress and decrease in the breaking elongation of SS wire with TiN ion plating**

The tensile strength, 0.2% proof stress, modulus of elasticity, and breaking elongation were obtained by tensile test (Fig. 5). For the SS wires, the tensile strength and 0.2% proof stress of the TiN coated wires were higher than those of the non-coated wires (Figs. 5A, B). However, the breaking elongation was decreased after TiN coating, and no significant difference was found between the modulus of elasticity of the TiN coated and non-coated SS wires (Figs. 5C, D).
Fig. 3 Representative polarization curves obtained by anodic polarization test. Representative polarization curves of SS (A) and Ni-Ti (B) wires from anodic polarization tests in 0.9% NaCl solution at 37°C. Dashed line: Non-coated wires, solid line: TiN coated wire.

Fig. 4 Surface observation of SS and Ni-Ti wires in anodic polarization test using optical microscope. Representative surface of non-coated SS wire (upper left), TiN coated SS wire (upper right), non-coated Ni-Ti wire (lower left), and TiN coated Ni-Ti wire (lower right) (magnification 200×); scale bar=50 µm. Black arrow points to a pitting corrosion. (A) At the slightly higher potential than the breakdown potential of the non-coated wire. SS wire: 0.5 V, Ni-Ti wire: 1.4 V. (B) At the end of anodic polarization test. SS wire: 1.0 V, Ni-Ti wire: 2.0 V.
Fig. 5 Comparison of physical properties obtained in tensile tests.
Tensile strength (A), 0.2% proof stress (B), modulus of elasticity (C), and breaking elongation (D) of non-coated SS wire and TiN coated SS wire determined by tensile tests. *p<0.05.

Increase in the flexural rigidity of the SS wire and decrease in the bending force of Ni-Ti wire with TiN ion plating
Representative bending plots and mean load values for each wire obtained via bending tests are shown in Figs. 6 and 7, respectively. For the SS wires, the flexural rigidity and 0.1 mm offset bending strength of the TiN coated wires were higher than those of the non-coated wires (Figs. 7A, B). For the Ni-Ti wires, the unloading bending forces of the TiN coated wires at deflections of 3.0, 2.0, 1.0, and 0.5 mm were lower than those of the non-coated wires (Fig. 7C). At 1.0 and 0.5 mm deflection points, the unloading bending force of TiN coated wires was less than half those of the non-coated wires.

Fig. 6 Representative 3-point bending test results for TiN coated and non-coated wires.
Representative force-deflection curves for non-coated SS wire and TiN coated SS wire (A), non-coated Ni-Ti wire and TiN coated Ni-Ti wire (B).

Decrease in the friction force of orthodontic wire with TiN ion plating
The result of friction test for different combinations of bracket/wire/angulation is shown in Fig. 8. In angulations of 0 degrees, the friction forces of the TiN coated Ni-Ti wires were lower than those of the non-coated Ni-Ti wires. In angulations of 10 degrees, the friction forces of the TiN coated SS and Ni-Ti wires were lower than those of the non-coated SS and Ni-Ti wires, respectively.

DISCUSSION
In the present study, the breakdown potentials of the TiN coated SS and Ni-Ti wires were increased and the current densities at the passive region of TiN coated SS and Ni-Ti wires were decreased in the anodic polarization test. These results suggest that the corrosion resistance of the orthodontic wire was improved by TiN coating. The surfaces of TiN coated wires exhibited less large pitting than the surfaces of non-coated wires, in accordance with the results of the electrochemical tests. Thus the corrosion resistance of the orthodontics wire was increased by the TiN ion plating.
The alignment of teeth in orthodontic treatment is carried out by exploiting the mechanical properties of the wire used. In general, SS wire is applied to finishing orthodontic treatments using multi bracket appliances. Therefore, high breaking strength and stiffness is needed for such SS wires. In this work, the mechanical tests, including tensile and bending tests, were conducted referring to JIS-T6530. The TiN ion plating was found to increase the tensile strength and 0.2% proof stress of the SS wire, and decreased its breaking elongation. The flexural rigidity and 0.1 mm offset bending strength of the SS wire were also increased. These results indicate that the tensile strength and stiffness of the SS wire were increased by the TiN ion plating. Therefore, TiN coated SS wire is expected to be useful for finishing orthodontic treatments. Ni-Ti wire is used for the initial treatment of dental arch alignment, and therefore suitable bending force and maintenance of power is important for Ni-Ti wires. It was found that the load value at each displacement point of TiN coated Ni-Ti wire was decreased. The TiN ion plating also reduced the unloading bending force of the Ni-Ti wire. Although the TiN coated Ni-Ti wire still had super-elastic and shape memory properties, the properties of Ni-Ti wire were decreased. TiN indicates higher tensile strength, higher stiffness, and lower elasticity than SS. However, it is unlikely that the TiN layer mainly leads to these results, because it is a thin layer. Several studies have reported that mechanical properties of SS and Ni-Ti wires are changed by heating treatment\(^{18-21}\). In this study, orthodontic wires were heated at 220°C for 7 min for TiN coating. For clarifying the effect of heating, we heated the Ni-Ti wire at 220°C for 7 min without TiN coating (heating non-coated Ni-Ti wire) and compared
the bending force of heating non-coated Ni-Ti wire and non-coated Ni-Ti wire. The unloading bending force of heating non-coated Ni-Ti wires at deflections of 3.0, 2.0, 1.0, and 0.5 mm were 2.86±0.04, 1.79±0.04, 1.55±0.03, and 1.39±0.06 N. These force were lower than those of the non-coated Ni-Ti wires (p<0.05) and higher than those of the TiN coated Ni-Ti wires (p<0.05). This result indicated that the changes of the mechanical properties might be caused by heating and TiN coating. Therefore, finding coating conditions against reduction of elasticity is needed to improve the properties of TiN coated Ni-Ti wire.

The orthodontic wires could be also damaged by friction between wires and brackets. We found that the friction forces of the TiN coated SS and Ni-Ti wires were lower than those of the non-coated SS and Ni-Ti wires in the angulations 10 degrees metal and plastic brackets. In addition, the friction forces of the TiN coated Ni-Ti wires were lower than those of the non-coated Ni-Ti wires in the angulations 0 degree both brackets. The Ra of SS and Ni-Ti wires almost did not change. However, frictional coefficient is different for each kind of material. In this study, the material of wire surface was changed with TiN by ion plating. It has been reported that frictional coefficient of dental instruments surface was reduced by TiN coating. There is possibility that frictional coefficient was decreased by changing metal of surface into TiN by ion plating2. Sliding mechanics is widely used in orthodontics therapy. The friction at surface between bracket and wire may interrupt to get demanding to the movement. The low level of friction may increase tooth movement efficiently. Therefore, the low friction wires are desired. TiN coating get low friction, suggesting that TiN coated wire could be useful in orthodontics treatment.

CONCLUSION

The present study has demonstrated that TiN coating by ion plating improves the corrosion resistance of orthodontic wire. Furthermore, the tensile strength and stiffness of SS wire were increased after TiN coating, suggesting that TiN coated SS wire could be particularly useful for orthodontic treatment. In contrast, the unloading bending force of TiN coated Ni-Ti wire was decreased. In other words, its elastic force was decreased. In addition, TiN coating provided low friction forces.

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REFERENCES