Effects of Titanium Nitride Coatings on Surface and Corrosion Characteristics of Ni-Ti Alloy

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The structure of a titanium nitride film coated by arc ion plating on a Ni-50Ti shape memory alloy was characterized by X-ray photoelectron spectroscopy (XPS). The corrosion behavior of the titanium nitride-coated Ni-50Ti alloy was examined in 0.9% NaCl solution by potentiodynamic polarization measurements and a polarization resistance method. XPS spectra showed that the titanium nitride film consisted of three layers, a top layer of TiO2, a middle layer of TiNx (x > 1), and an inner layer of TiN. The passive current density for the titanium nitride-coated alloy was approximately two orders of magnitude lower than that of the polished alloy in the potential range from the free corrosion potential to +500 mV (vs. Ag/AgCl). Pitting corrosion associated with breakdown of the coated film occurred above this potential. The polarization resistance data also indicated that the corrosion rate of the titanium nitride-coated alloy at the free corrosion potential (+50 to +100 mV) was more than one order of magnitude lower than that for the polished alloy.

Key words: Titanium alloy, XPS, Corrosion resistance

INTRODUCTION

The Ni-Ti shape memory alloy has been used clinically for surgical implants1-2. This alloy, however, contains approximately 50 at% of nickel which is a hapten most frequently involved in hypersensitivity reactions. Although most in vitro cytotoxicity tests and histological studies have shown good biocompatible characteristics of the Ni-Ti shape memory alloy3,4, the corrosion resistance must be improved to reduce nickel release.

In recent years, corrosion-resistant titanium nitride coating has been applied to various structural materials in order to increase corrosion resistance in high temperature water or in strong acid solutions5,6. Takahashi and Hayashi7 demonstrated that a titanium nitride layer markedly inhibited active dissolution of Ti in 20% HCl and H2SO4 solutions. Taguchi et al.8 examined the corrosion behavior of titanium nitride powders of various compositions in 1 kmol·m-3 H2SO4 solution and found that corrosion was apparently inhibited when the nitrogen content of titanium nitride was more than 40 at%. With Ni-Ti shape memory alloys for dental and medical applications, the effect of titanium nitride coating on the anodic corrosion behavior in 1% NaCl solution was investigated by Kimura and Sohmura9. They reported that the anodic current density at 2000 mV (vs. SCE) was drastically reduced by three orders of magnitude with a titanium nitride coating prepared by the HCD process.
Little is known, however, concerning the corrosion rate of Ni-Ti alloy with a titanium nitride coating freely immersed in a simulated physiological solution. With regard to the biocompatibility as an implant material, it is necessary to assess the surface structure of the titanium nitride film on the Ni-Ti alloy.

In the present study, the Ni-50Ti alloy was coated with titanium nitride film by arc ion plating, and the chemical composition of the top few atomic layers, which is expected to strongly influence the initial cell adhesion, was determined by X-ray photoelectron spectroscopy (XPS). In addition to anodic polarization measurements, the corrosion rate of the Ni-50Ti alloy both with and without titanium nitride coating at a free corrosion potential was estimated in 0.9% NaCl solution using a polarization resistance method.

**MATERIALS AND METHODS**

**Sample preparation**
The Ni-50Ti alloy polished with 1 μm alumina paste was subjected to titanium ion sputtering at $3 \times 10^{-3}$ Pa for 60 s to remove the surface oxide layer. The titanium nitride film was coated by arc ion plating at 400°C under a N$_2$ atmosphere for 20 min. The pressure in the chamber was 1 Pa. After ion plating, the sample was cooled to below 200°C and removed from the chamber. Some specimens were heated in an electric furnace at 400°C for 10 min to examine the influence of heat treatment in controlling the transformation temperature of the alloy on the chemical composition of the coated thin film surface and its corrosion protection properties.

**Characterization of coated TiN film**
The surface and cross-sections of the coated film were examined by scanning electron microscopy (SEM). Identification and the crystallographic features of the coated layer were investigated by X-ray diffractometry (XRD). An X-ray diffractometer* with Ni-filtered Cu K$_\alpha$-radiation was used. The Cu K$_\alpha$-radiation was generated with a 35 kV accelerating voltage and 20 mA anode current. The patterns were recorded with a scanning speed of 1° (2θ) • min$^{-1}$. The top few atomic layers of the coated surface were characterized by XPS. The XPS spectra were obtained using an X-ray photoelectron spectrometer** with Al K$_\alpha$-radiation (energy 1486.6 eV) at 7 kV accelerating voltage and 30 mA current under a pressure of $5 \times 10^{-7}$ Pa. The binding energy scale was calibrated by the Au 4f$_{7/2}$ and Cu 2p$_{3/2}$ peaks at 83.8 and 932.8 eV, respectively. To establish the layer structure of the titanium nitride film in the depth direction, the take-off angle of the photoelectrons was varied from 90° to 15°. Enhancement of surface sensitivity can be obtained with low-angle photoelectron exit from the surface. The film on the alloy was also subjected to argon ion sputtering to obtain the depth profile of each element. The etching rate was approximately 0.1 nm • s$^{-1}$ on pure silver. Curve fitting for multiple peaks in the spectra was performed with background subtraction and Gaussian shape fit programs#.

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* Geigerflex 2013, Rigaku Corp., Tokyo, Japan  
** ESCA-850, Shimadzu Co. Ltd., Kyoto, Japan  
# ESPAC-200, Shimadzu Co. Ltd., Kyoto, Japan
Evaluation of corrosion resistance

The anodic corrosion behavior of a polished and a titanium nitride-coated Ni-50Ti alloy was examined in 0.9% NaCl solution by potentiodynamic polarization measurements. The corrosion rate in the freely immersed condition was estimated by a polarization resistance method using the square wave current technique. The detailed experimental procedures for electrochemical measurements were described elsewhere\textsuperscript{10,11). All electrochemical measurements were performed at 37°C.

RESULTS AND DISCUSSION

Fig. 1 shows a cross-sectional view of the titanium nitride film coated on the Ni-50Ti alloy by arc ion plating. The thickness of the titanium nitride film was approximately 1-2 μm. Fig. 2 is an X-ray diffractogram of the film coated on the Ni-50Ti alloy, with diffraction peaks of TiN 111, 200, 220, 311, and 222. No peaks of TiO\textsubscript{2} or Ti\textsubscript{2}N were observed.

Fig. 3 shows the Ti 2p spectra from the surface of the titanium nitride film at the photoelectron take-off angles of (a) 90° and (b) 30°. Curve fitting for multiple peaks in the Ti 2p spectra suggested the presence of three titanium compounds. A peak at 458.5 eV corresponded to the Ti 2p\textsubscript{3/2} sublevels in TiO\textsubscript{2}\textsuperscript{12,13}, and one at 455.3 eV was attributed to TiN\textsuperscript{12,13}. The peak at 456.8 eV, 1.5 eV on the higher binding energy side of TiN, was assigned to a titanium nitride with lower electron density than the Ti in TiN. It was
demonstrated by Porte et al. and Terashima et al. that charge transfer from titanium to nitrogen increased with increases in nitrogen atom concentration in TiNx, resulting in a shift of the Ti 2p peak to the higher binding energy side. Considering this, the Ti 2p3/2 peak at 456.8 eV may be assigned to a hyperstoichiometric mononitride, TiNx (x>1). Curve fitting with a Gaussian shape fit program showed that the Ti 2p3/2/Ti 2p1/2 intensity ratio varied with the valency of titanium. As noted previously by Yabe, this is partly because the intensity of the satellite lines at the higher binding energy side of Ti 2p doublet lines vary with the valency of titanium.

There was a relative enhancement of TiO2 spectral intensity at 458.5 eV with the 30° photoelectron take-off angle, indicating that the surface of the titanium nitride film was oxidized when the sample was exposed to air. The Ti 2p3/2 spectrum intensity of TiNx at the 30° take-off angle was relatively higher than that of TiN at 90°, while it was relatively lower at 90°. These results suggest that the titanium nitride film consisted of three layers, a top layer of TiO2, a middle layer of TiNx, and an inner layer of TiN. This is consistent with the results reported by Miyagi et al. obtained for a titanium nitride surface formed on a pure titanium in a N2 stream at 1000°C for 4 h.

Fig. 4 shows the N ls spectra obtained from the surface of the titanium nitride film. The main peaks at 397.1 eV in both Figs. 4 (a) and (b) were attributed to TiN. The N ls peak position for TiNx shifted 1.3 eV to the lower binding energy side with respect to TiN. The Ti 2p3/2 spectrum intensity for TiNx obtained at the 30° take-off angle was slightly higher than that for TiN. The N ls spectral intensity for TiNx, however, was lower than that for TiN even though the nitrogen content in the titanium nitride was higher with TiNx (x>1). This may be explained by the strong satellite structure of stoichiometric TiN at around 2.2 eV on the higher binding energy side of the Ti 2p doublet lines. This satellite overlapped...
Fig. 3  Ti 2p spectra from the surface of the titanium nitride film at the photoelectron take-off angles of 90° (a) and 30° (b).
Solid line : measured spectrum,
dotted lines : each separated component spectrum,
chained line : sum of component spectra.
Fig. 4  N ls spectra from the surface of the titanium nitride film at the photoelectron take-off angles of 90° (a) and 30° (b).
Solid line : measured spectrum,
dotted lines : each separated component spectrum,
chained line : sum of component spectra.
the Ti 2p$_{3/2}$ line of TiN$_x$ and made the apparent intensity of the Ti 2p$_{3/2}$ line for TiN$_x$ higher than the actual intensity.

The minor peak at 398.6 eV could be assigned to adsorbed NH$_3$\textsuperscript{17),} which was generated by the reaction of TiN with air moisture occurring when the sample was removed from the reaction chamber,

\[ 2 \text{TiN} + 4 \text{H}_2\text{O} \rightarrow 2 \text{TiO}_2 + 2 \text{NH}_3 + \text{H}_2 \]  

The minor peaks at 400.1 eV and 401.8 eV could be attributed to adsorbed N$_2$\textsuperscript{13}) and NO\textsuperscript{12)}, respectively. These adsorbed species could be generated by reactions between the TiN film and oxygen in air,

\[ 2 \text{TiN} + 2 \text{O}_2 \rightarrow 2 \text{TiO}_2 + \text{N}_2 \]  
\[ \text{TiN} + 3/2 \text{O}_2 \rightarrow \text{TiO}_2 + \text{NO} \]  

The surface of the TiN film was oxidized to produce a TiO$_2$ on the topmost surface.

Fig. 5 shows the Ti 2p (a) and N ls (b) spectra obtained from the titanium nitride surface after heating in air at 400 °C for 10 min. The Ti 2p spectrum indicates that the titanium on the surface was mainly in the form of TiO$_2$. The small peak at 455.3 eV was attributed to TiN$_x$ under the oxide layer. A striking feature of the N ls spectrum was the relative enhancement of the peak intensity at around 402 eV compared with the N ls spectrum in Fig. 4 (b). This peak could be assigned to adsorbed NO, indicating that the oxidation of titanium nitride during the heat treatment mainly proceeded as reaction (3).

Fig. 6 shows the Ni 2p spectra as a function of argon ion sputtering time from the titanium nitride film on the Ni-50Ti alloy after heat treatment at 400 °C for 10 min. No nickel was detected in the surface layer down to at least 100 nm from the top surface.

Fig. 7 shows the anodic potential/current density curve in 0.9% NaCl solution for the polished Ni-50Ti alloy, the titanium nitride-coated alloy, and the titanium nitride-coated alloy with heat treatment at 400 °C for 10 min. A wide passive region was observed for the polished alloy at potentials from −200 mV to +1200 mV, where the passive current density ($i_p$) was approximately 2 $\mu$A · cm$^{-2}$. For the titanium nitride-coated alloy, the free corrosion potential was about 400 mV more positive than that of the polished alloy. Passivation was observed at potentials from −50 mV to +500 mV with an $i_p$ value of 0.04 $\mu$A · cm$^{-2}$, approximately two orders of magnitude lower than the value for the polished alloy. Above +500 mV, there was an abrupt increase in current density with further polarization up to 520 mV, with a further plateau between 520 mV and 675 mV at a constant current density of 0.35 $\mu$A · cm$^{-2}$. The current density increased again at potentials above +675 mV. There were no significant differences in the anodic polarization behavior of the titanium nitride-coated alloys with and without heat treatment.

Fig. 8 shows the secondary electron images of the titanium nitride-coated alloy surface after recording of the anodic polarization measurements from the free corrosion potential to +1500 mV. There were many small corrosion product deposits on the titanium nitride film which were not identified by XRD, and these were assumed to be TiO$_2$. Clearly visible cracks propagated in the titanium nitride film as indicated by arrows in Fig. 8 (a), and some of the film peeled off the underlying alloy (area A). There were pits propagating deep into the alloy at places where the film had peeled off (Fig. 8 (b)).

At +500 mV, mechanical cracking of the titanium nitride film seemed to take place,
facilitating the anodic dissolution process at the alloy surface exposed to the solution. The mechanical cracking of the protective film is not fully understood, but breakdown of the passivity has been reported for zirconium and aluminum in chloride media with apparent cracking of the protective film\(^{18}\). The oxide film formation associated with the anodic dissolution led to repassivation of the alloy in the +500 mV to +675 mV potential range.
Breakdown of the film, however, occurred at much lower potentials than the breakdown potential of 1200 mV for the polished alloy. The reason may be that chloride and hydrogen ions concentrated in the cavities which were formed by the peeling off of the titanium nitride film.

Fig. 9 shows variations in polarization resistance \( (R_{\text{corr}}) \) with time for the polished and the titanium nitride coated Ni-50Ti alloy in 0.9% NaCl solution. The \( R_{\text{corr}} \) parameter is inversely proportional to the corrosion rate of metals and alloys. The \( R_{\text{p}} \) value for the titanium nitride-coated alloy was more than one order of magnitude higher than that for the polished alloy, indicating that the corrosion rate at the free corrosion potential (approximately +50 – +100 mV) was drastically reduced by the titanium nitride coating.

The topmost layer of the titanium nitride film coated on the Ni-50Ti alloy by arc ion plating was found to be composed of TiO\(_2\), which is chemically identical to the surface film on pure titanium. The corrosion rate of the Ni-50Ti alloy freely immersed in 0.9% NaCl solution was reduced by more than one order of magnitude with the titanium nitride coating. In addition, the titanium nitride film did not contain any nickel, suggesting that the amount of nickel released would be far less than with the polished Ni-50Ti alloy. The heat treatment to control the transformation temperature after the titanium nitride coating increased
Fig. 7  Anodic potential/current density curve in 0.9% NaCl solution.  
Dashed line : polished Ni-50Ti alloy,  
solid line : titanium nitride-coated alloy,  
dotted line : titanium nitride-coated alloy with heat treatment at 400°C for 10 min.

Fig. 8  Secondary electron images of the titanium nitride-coated alloy surface after the anodic polarization measurements from the free corrosion potential to +1500 mV in 0.9% NaCl solution.
the thickness of surface TiO₂ film, but did not change the anodic polarization behavior. Considering the chemistry of the coated surface film and the improved corrosion resistance, the biocompatibility of the titanium nitride-coated Ni-50Ti alloy as an implant material is expected to be comparable to that of a pure titanium unless highly polarized anodically in vivo.

CONCLUSION

The titanium nitride coating prepared by the arc ion plating method improved the corrosion resistance of the Ni-50Ti shape memory alloy in the potential range from the free corrosion potential to +500 mV, but pitting corrosion associated with breakdown of the coated film occurred above this potential in 0.9% NaCl solution. Corrosion rate of Ni-50Ti alloy can be reduced by more than one order of magnitude by titanium nitride coating, unless the alloy is highly polarized anodically in vivo. The top surface of the TiN film was found to be TiO₂, which is chemically identical to the surface film on pure titanium.

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REFERENCES


白歯部と前歯部用コンポジットレジンの水中浸漬下のクリープ
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市販の白歯部用コンポジットレジンと前歯部用コンポジットレジンの各2種類について、その圧縮クリープと回復について水中浸漬下で研究した。
試験した白歯部用コンポジットレジンの500時間後のクリープひずみは8.3kgf/mm²の応力下では1%未満であった。この結果、これから白歯部用コンポジットは咬合応力に十分耐え得ることを示していた。前歯部用コンポジットレジンではフィラー含有量が白歯部用に比べて少ないため、白歯部用にくらべてクリープひずみが大きかった。コンポジットの回復は試験直後に著しく大きかった。500時間後のクリープ試験後の試料の吸水率は、白歯部用コンポジットレジンでは、ある低応力下ではほぼ一定であった。

グラスアイオノマーセメントの機械的性質の比較
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三種のグラスアイオノマーセメントを選びまして機械的性質測定し、各セメントの特性を検討することにより、今後の材料開発の参考とした。三種のセメントのうち一種は、ガラス繊維を含有した自硬化性の試作材料で、他の二種は市販の自硬化性および光照射型セメントであった。バイアクシャルまたは通法の三点曲げ試験をおこない、後者からは弾性係数も求めた。37℃、相対湿度100％で24時間保存した試料を室温で試験した。市販のセメントが典型的な脆性破壊を示したのに対し、繊維を含有した試作材料では、破壊過程を著しく遅延する効果が認められ、これはワイルド係数が大きくなること、すなわちより安定した破壊挙動につながった。市販のセメントで得られた特性は、象牙質に近似した弾性率と歯科用複合レジンに匹敵する強度であった。

アークイオンプレーティング法により Ni-50Ti 合金上に創成した TiN 膜の表面性状と耐食性
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アークイオンプレーティング法によりインプラント用 Ni-50Ti 合金上に創成した窒化チタン薄膜の構造と耐食性を調べた。X線光電子分析装置を用いた角度分析により、窒化膜は2層構造を示しており、最表面から TiO₂、TiN、（x > 1）の二層構造が変化していることが明らかとなった。また、コーティング層からニッケルが検出されなかった。0.9 % NaCl溶液中におけるアノード分極曲線を測定したところ、窒化チタンでコーティングした Ni-50Ti 合金の不動態保持電流は自然浸没電位から+500mV（vs. Ag/AgCl）では研磨状態の合金と比較しておよそ1/100 となり、耐食性が向上することが明らかとなった。しかし、脱不動態化電位が研磨状態の+1200mVから+500mVに低下し、孔食感受性が高くなった。分極抵抗の測定から、自
急速加熱型せっこう系埋没材と鍛造体の性状

第1報 クラウンの表面性状と適合性

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鍛造の短時間化を目的として，急速加熱型せっこう系埋没材が開発された。この埋没材で作製した鍛造体を，埋没材の鍛造開始から30分後に700℃の炉内に入れ，30分加熱するだけで鍛造できるものである。本研究では3種類の市販品について，膨張特性ならびに耐熱性との関連から鍛造クラウンの表面性状および適合性を調べた。鍛造した埋没材をブロックを作製し，鍛造開始から30分後に700℃の炉内で急速加熱すると，従来型のクリスタルライト埋没材は炉内に入れて間もなく粉々に破壊してしまったが，急速加熱型埋没材ではまったく破壊は生じない。生じても小さなものであった。この試験で小さなクラックが生じた埋没材においてのみ，クラウンのマージンにわずかなバリが生じることがあったが，全面的にバリの発生は少なかった。鍛造体の表面あらえに大きな影響はみられなかった。急速加熱した際の熱膨張量には用いた3種類の埋没材間でほとんど差は認められなかったが，鍛造開始から30分後の硬化膨張は著しく異なっており，従来の鍛造法の場合と同様に，クラウンの良好な適合性を得るには鍛造開始前の硬化膨張値が大きな埋没材ほど有効であることがわかった。

Bis-GMA および iso-Bis-GMA の NMR スペクトル

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Bis-GMA はコンポジットレンジンやそのボンディング剤のモナリサシステムに歯科では広く用いられている。Bis-GMA は精製されていないので，末反応原料や合成過程に生ずる種々の不純物が含まれている。本研究は市販Bis-GMA から HPLC により Bis-GMA および iso-Bis-GMA を分離分取した。さらに，DEPT や COSY スペクトルにより両モノマーのプロトン及びカーボンのシグナルの帰属を行ったものである。