

## 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 TiO<sub>2</sub>, a middle layer of TiN<sub>x</sub> ( $x > 1$ ), 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–+100 mV) was more than one order of magnitude lower than that for the polished alloy.

Key words: Titanium alloy, XPS, Corrosion resistance

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### INTRODUCTION

The Ni-Ti shape memory alloy has been used clinically for surgical implants<sup>1,2</sup>. 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 alloy<sup>3,4</sup>, 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 solutions<sup>5,6</sup>. Takahashi and Hayashi<sup>7</sup> demonstrated that a titanium nitride layer markedly inhibited active dissolution of Ti in 20% HCl and H<sub>2</sub>SO<sub>4</sub> solutions. Taguchi *et al.*<sup>8</sup> examined the corrosion behavior of titanium nitride powders of various compositions in 1 kmol · m<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> 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 Sohmura<sup>9</sup>. 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  $\mu\text{m}$  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  $\text{N}_2$  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  $1^\circ (2\theta) \cdot \text{min}^{-1}$ . 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  $90^\circ$  to  $15^\circ$ . 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  $0.1 \text{ nm} \cdot \text{s}^{-1}$  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<sup>10,11</sup>. 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-50 Ti alloy by arc ion plating. The thickness of the titanium nitride film was approximately 1-2  $\mu\text{m}$ . 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  $\text{TiO}_2$  or  $\text{Ti}_2\text{N}$  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<sub>3/2</sub> sublevels in  $\text{TiO}_2$ <sup>12,13</sup>, and one at 455.3 eV was attributed to TiN<sup>12,13</sup>. 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

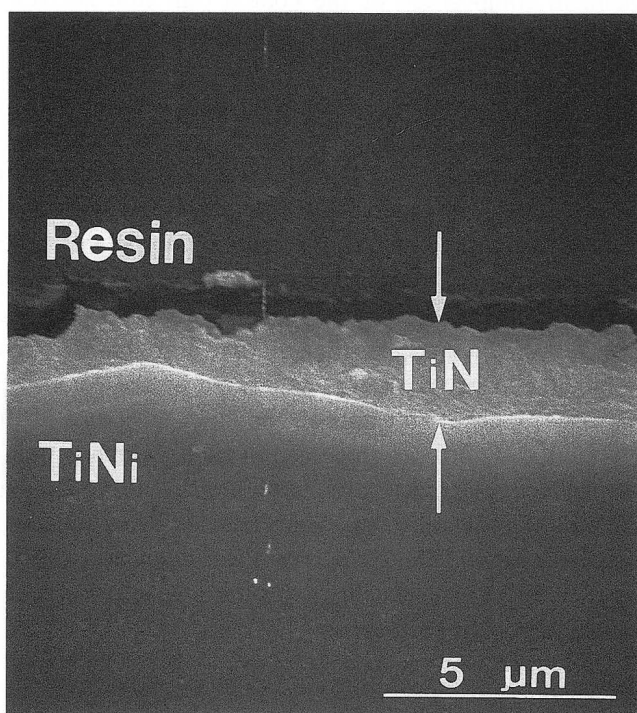


Fig. 1 Cross-section of the titanium nitride film coated on the Ni-50Ti alloy by arc ion plating.

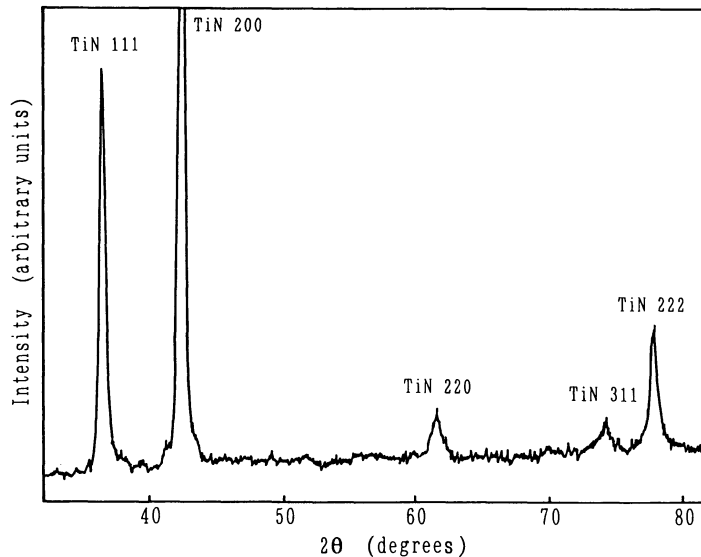


Fig. 2 X-ray diffractogram of the titanium nitride film coating on the Ni-50Ti alloy.

demonstrated by Porte *et al.*<sup>14)</sup> and Terashima *et al.*<sup>15)</sup> that charge transfer from titanium to nitrogen increased with increases in nitrogen atom concentration in  $\text{TiN}_x$ , resulting in a shift of the Ti 2p peak to the higher binding energy side. Considering this, the Ti 2p<sub>3/2</sub> peak at 456.8 eV may be assigned to a hyperstoichiometric mononitride,  $\text{TiN}_x$  ( $x > 1$ ). Curve fitting with a Gaussian shape fit program showed that the Ti 2p<sub>3/2</sub>/Ti 2p<sub>1/2</sub> intensity ratio varied with the valency of titanium. As noted previously by Yabe<sup>16)</sup>, 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  $\text{TiO}_2$  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 2p<sub>3/2</sub> spectrum intensity of  $\text{TiN}_x$  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  $\text{TiO}_2$ , a middle layer of  $\text{TiN}_x$ , 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  $\text{N}_2$  stream at 1000°C for 4 h<sup>12)</sup>.

Fig. 4 shows the N 1s 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<sup>12)</sup>. The N 1s peak position for  $\text{TiN}_x$  shifted 1.3 eV to the lower binding energy side with respect to TiN. The Ti 2p<sub>3/2</sub> spectrum intensity for  $\text{TiN}_x$  obtained at the 30° take-off angle was slightly higher than that for TiN. The N 1s spectral intensity for  $\text{TiN}_x$ , however, was lower than that for TiN even though the nitrogen content in the titanium nitride was higher with  $\text{TiN}_x$  ( $x > 1$ ). 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<sup>14)</sup>. This satellite overlapped

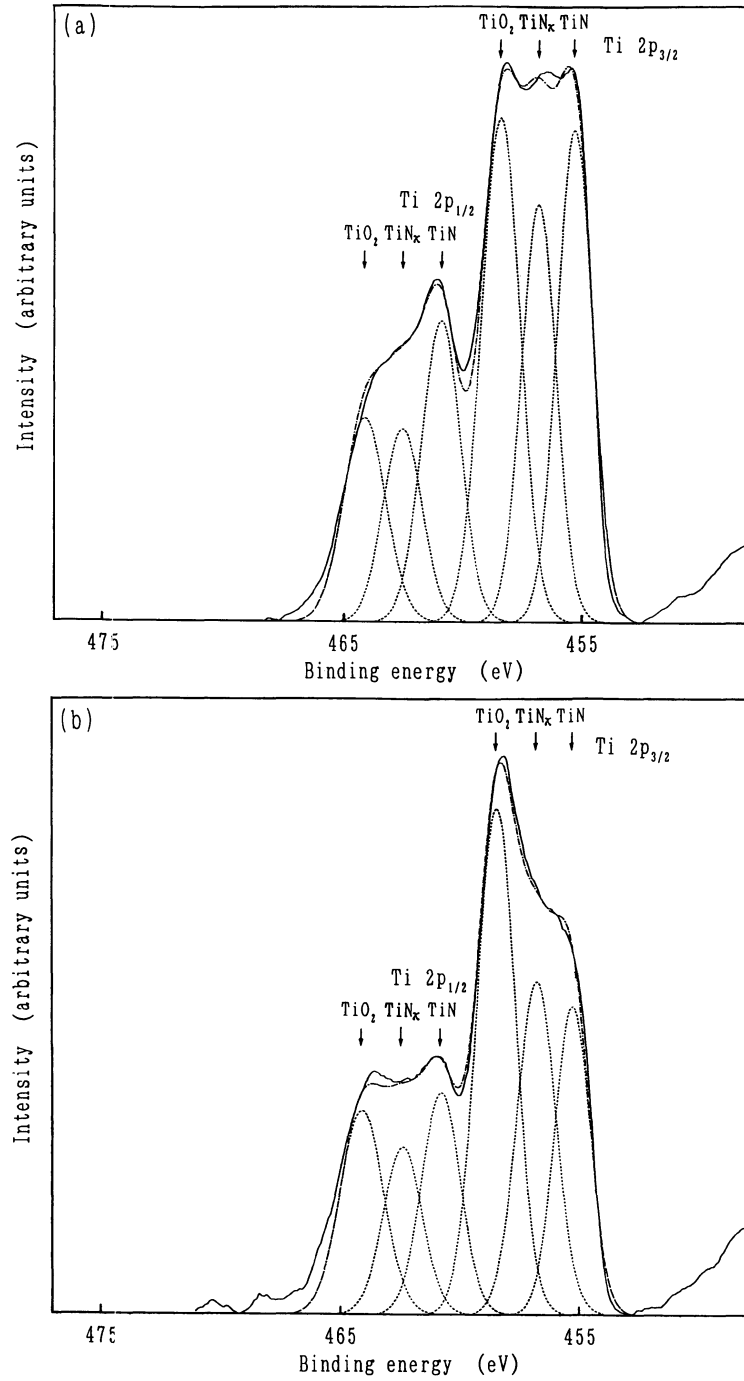


Fig. 3 Ti 2p spectra from the surface of the titanium nitride film at the photoelectron take-off angles of 90° (a) and 30° (b).  
 Solid line : measured spectrum,  
 dotted lines : each separated component spectrum,  
 chained line : sum of component spectra.

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