Title	Evaluation of Plasma Ion Beam Sputtered TiN/TiAlN Multilayers on Steel for Bio Implant Applications
Author(s)	Balasubramanian, Subramanian; Guruswamy, Brindha; Takahashi, Makoto et al.
Citation	Transactions of JWRI. 2011, 40(2), p. 55-58
Version Type	VoR
URL	https://doi.org/10.18910/4553
rights	
Note	

Transactions of JWRI, Vol.40 (2011), No. 2

Evaluation of Plasma Ion Beam Sputtered TiN / TiAlN Multilayers on Steel for Bio Implant Applications†

BALASUBRAMANIAN Subramanian*, GURUSWAMY Brindha ***, TAKAHASHI Makoto*, NISHIKAWA Hiroshi *, and KOBAYASHI Akira ***

Abstract

Layers of 1.2 µm thick TiN / TiAlN were deposited onto 316L stainless steel substrates by a plasma ion beam sputtering technique. The layers were sputtered in pure Ar and N_2 with the ion beam voltage of 1 keV and ion beam current of 30mA. Polycrystalline nature with FCC structure was identified from XRD analysis. The presence of Ti, Al, C and N elements on the surface of the film was confirmed by the XPS survey spectrum taken on the surface of the coatings. The Ti2p region can be decomposed into several contributions corresponding to the different oxidation states of titanium. The columnar nature of growth was observed from the cross sectional HRTEM analysis. The nano-hardness of the TiN/TiAlNcoatings were found to be 30 GPa. The superior corrosion resistance in simulated body solution environment was observed for the multilayer coated specimen.

KEY WORDS: (Surface modification), (Multilayers), (Nanoindentation), (Plasma ion beam sputtering)

1. Introduction

Ti-based alloys are widely used for orthopedic implants because of the superior biocompatibility of titanium and its high corrosion resistance. However, Ti is a soft material with a low shear resistance of the surface, that should be mainly due to the naturally formed oxide, and thus, hardening of the titanium surface is performed [1-3]. Titanium and its alloy have been popularly used to make artificial heart valves. When the titanium oxide film is deposited on the titanium artificial heart valves, since the valves would open and close billions of times in a human body, the film must have reliable mechanical properties besides good blood compatibility. It is known that titanium nitride has superior mechanical, chemical and corrosion properties, such as high hardness, good wear resistance, corrosion resistance and chemical stability. Titanium nitride (TiN) is an extremely hard, conducting ceramic material, often used as a coating material for metal components to improve their surface properties [4]. The idea of TiN/ TiAlN multilayer films is to combine the advantages of TiN and TiAlN.

Several techniques have been used for the preparation of these nitride superlattice hard coatings such as physical vapor deposition (PVD) and chemical vapor deposition (CVD) [5-8]. The application of sputtering facilitates the production of dense and well-adhered films with controlled elemental composition [9]. Among the sputtering techniques, the plasma ion beam sputtering is widely used because of its lower deposition temperature, higher stability and higher film density. The surface of the sputter target is often oxidized or nitrided during reactive sputtering in an atmosphere of N_2 or O_2, and is the main cause of reduction in deposition rate. Therefore it is important to separate the target and the substrate holder as in ion beam sputtering method so that the reactive gas cannot get close to the target. Since the materials are directly sputtered onto the substrate, the process can be precisely controlled so that the films can be deposited with extremely high accuracy and repeatability.

In this paper we have investigated the effect of ion beam sputtered TiN / TiAlN multilayered coatings on improving the corrosion resistance of 316L stainless steel in simulated bodily fluid and its surface characteristics are discussed briefly.

2. Experimental

Multilayers of TiN / TiAlN with bilayer thickness of 30 nm and total thickness of 1.2 µm were prepared by plasma ion beam sputtering technique using HOUEI vacuum system on to Si (100) wafer, and AISI 316L stainless steel substrates. The layers were sputtered in pure Ar and N_2 for a sputtering time of 5hrs. A rotational target holder was used to obtain a layered structure. The total thickness of the coating was controlled by the deposition time. The modulation wavelength of the multilayer coatings can be calculated from the XRD data using the following equation [10]:

$$\Lambda = \frac{\pm m\lambda}{2(\sin\theta_{SR} - \sin\theta_{PR})} \qquad \text{-------- (1)}$$

---

† Received on December 26, 2011

***Central Electrochemical Research Institute, India (BS)
***Alagappa Polytechnic College, India (G.Brindha)

Transactions of JWRI is published by Joining and Welding Research Institute, Osaka University, Ibaraki, Osaka 567-0047, Japan

Where m is the order of the satellite reflection, θ_{PR} is the position of the principal Bragg reflection, θ_{SR} is the position of the satellite reflection and λ is the wavelength of the X-rays. The total numbers of layers were about 120 with the bilayer thickness of 100 Å. The total thickness of the coating was about 1.2 μm. The deposition parameters are summarized in **Table1**. The crystal structure of the coatings was examined by XRD using PANalytical-3040 X'pert pro diffractometer. The chemical nature of the outermost part of the films was obtained by X-ray photoelectron spectroscopy (XPS) using Multilab 2000. The XPS measurements were performed at a base pressure of 10^{-8} Torr using MgKα (X-ray of 1253.6 eV source). Thesurface morphology of the films was studied using a field emission scanning electron microscope (FESEM, sirion FEI). Nanoscale studies of the structure and the surface roughness of the deposited films were also investigated by atomic force microscopy (AFM). The Raman spectroscopy measurements used an excitation wavelength of 632.8 nm. The data were collected with a 10s data point acquisition time in the spectral region of 200–1000 cm^{-1}. The nano mechanical tests were investigated by means of a Nano Test, Micro Materials Ltd, UK.

3. Results

3.1 Structural and compositional analysis

The X-ray diffraction patterns of plasma ion beam sputtered TiN/TiAlN multilayer coatings are shown in **Fig.1.**The average grain size of the multilayer coatings calculated from Scherrer's formula [11] was found to be about 40 nm. It was found that the coatings exhibited face centred cubic structure for both single layers and multilayered coatings. TiN and TiAlN single layers are polycrystalline exhibiting diffraction peaks with the preferred orientation along (111) plane.The peak positions of TiAlN coatings are shifted to the higher angles with respect to TiN peaks owing to lattice constant decreases arise from the partial replacement of the titanium atoms in the TiN lattice by the aluminium.

Table1.

Parameter	Specification
Target (2"Dia)	Ti (99.99%)
Substrate	316L Stainless steel,
Substrate temperature	Room temperature
Target to substrate distance	75 mm
Ultimate vacuum	2 x 10^{-5} torr
Operating vacuu	2 x 10^{-4} torr
Ar:N	2 : 1
ArcVoltage	65 volts
Acceleration Voltage	1000 volts
Ion Beam current	30 Amps

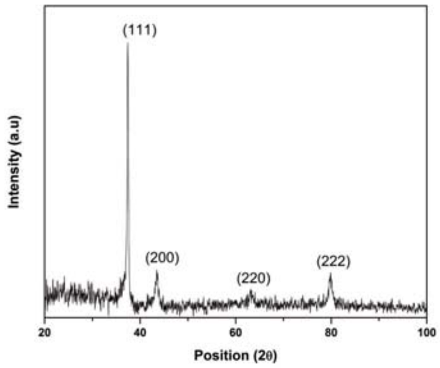

Fig.1 X-ray diffraction pattern of the ion beam sputtered TiN/TiAlN multilayer coatings.

The TiN/TiAlN multilayer coating also exhibited the B1-NaCl crystal structure. As expected, major diffraction peaks of (111), (200), (220) and (222) were observed in the XRD pattern. The use of X-ray photoelectron spectroscopy spectra allows for obtaining information on the chemical structure and bonding states in the outermost ~5 nm of the thin coating. XPS spectra of TiN/TiAlN multilayer coatings are shown in **Fig.2.**

The analysis indicates that Ti, Al, N, O and C elements coexist in the deposited TiN/TiAlN films. The peak associated with Ti2p consists of two peaks centered at 457.7 (Ti 2p3/2) and 462.7 eV (2p1/2). The major contribution in centered at 73.6 eV, is assigned to Al 2p3/2 in Al_2O_3 bonds [12]. The main peak position of 396.5 eV corresponds to the N1s electron in TiN [13]. The other contribution of the N 1s core level, of the sample, centered at 398.6 eV, is assigned to N–Al bonding. The peak at 395.6 eV assigned to N-C bonding which is in the form of TiO_xN_y [14]. The O1s XPS peak of TiN/TiAlN multilayer coatings to be fitted by the five Gaussian curves centered at 529.0, 529.6, 530.3, 531.1 and 531.9 eV. The components centered at 529.0, 529.6 and 531.1 eV are assigned to TiO_2, Ti-O and Ti-O bulk, OH respectively [13].The C1s spectrum of as deposited films shows peaks at 284.8, 286.0 and 288.8 eV, which are assigned to C(or CH), C-N and C=O, respectively [15].

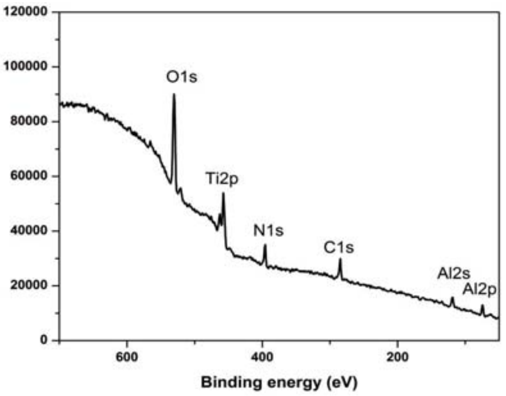

Fig.2 Survey XPS spectra of the TiN/TiAlN multilayer coatings.

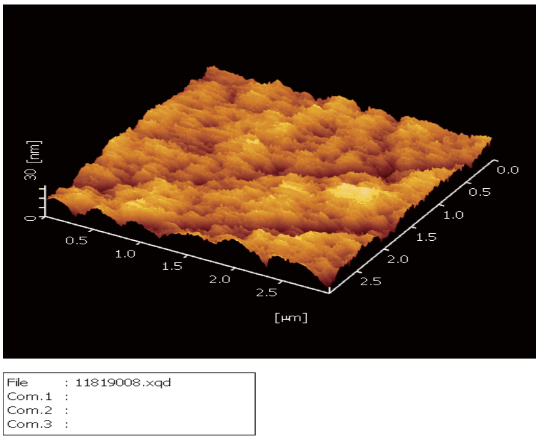

Fig.3 AFM image of the ion beam sputtered TiN/TiAlN multilayers.

3.2. Morphology and nanohardness

The three dimensional AFM image of the multilayer coatings is shown in **Fig.3.** It represents the hill like structure with the grain size of about 10-20 nm and the root mean square surface roughness factor was found to be 2.5 nm. The layer morphology of the multilayer coatings are analyzed from the bright field TEM micrograph of cross section analysis with HRTEM as shown in **Fig.4.** Distinct interfaces can be seen at the boundaries between the Si substrate and the first TiN layer being deposited. The microstructure of TiN/ TiAlN multilayer coatings consist of columnar grains with dimensions of ~ 50-70 nm in width. They are oriented in a way that the longer axes of the grains are parallel to the growth direction of the coating. The layered structure is pronounced due to the immiscibility of TiN and TiAlN layers. The columnar microstructure is typical of the films deposited at low temperature and low gas pressure in sputtering process. Typical load vs. displacement plots for the TiN/TiAlN multilayers deposited on stainless steel substrate are shown in **Fig.5** The total thickness of the multilayer coatings, are about 1.2 μm thick. It is generally accepted that the true indentation hardness of a thin film, without the influence of the substrate, is obtained when the indentation depth is <10% of the total film thickness.

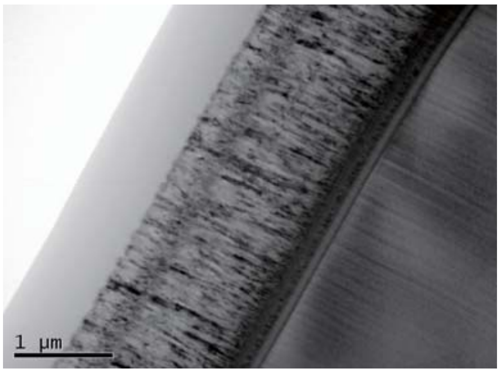

Fig.4 HRTEM image of the ion beam sputtered TiN/TiAlN multilayers.

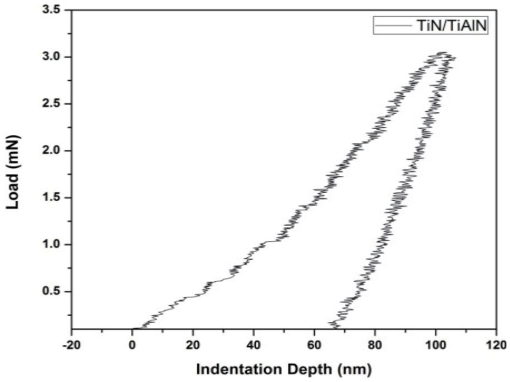

Fig.5 Load vs. displacement curves for the ion beam sputtered TiN/TiAlN multilayers.

In the current indentation results that were obtained at a maximum load of 1 mN, the indentation depths in the four samples are smaller than 100nm, i.e. below 10% of the total thickness of the coatings. Thus, the influence of the softer steel substrate is negligible.

The nanoindentation hardness of the coating, calculated from the load –indentation depth plot, was about 30 GPa whereas the single layer of TiN and TiAlN deposited under similar conditions showed hardnesses of about 22.2 and 19 GPa, respectively. With the introduction of TiN sublayers, the formation of lateral and radial cracks was suppressed as some of the energy was dissipated by deformation in the relatively ductile TiN sublayers.

3.3 Electrochemical corrosion in SBF

Potentiodynamic polarization curves of the TiN/TiAlN multilayer, TiAlN, TiN single layer coatings and the bare substrate are shown in **Fig.6**. The corrosion current density and the corrosion potential were obtained by the intersection of the extrapolation of anodic and cathodic Tafel curves. The E_{corr} of multilayer layer coated samples, when compared to the single layers and substrate, shows a shift towards the positive side. The positive shift of E_{corr} for TiN/TiAlN indicates better corrosion resistance of the TiN/TiAlN multilayer coatings.

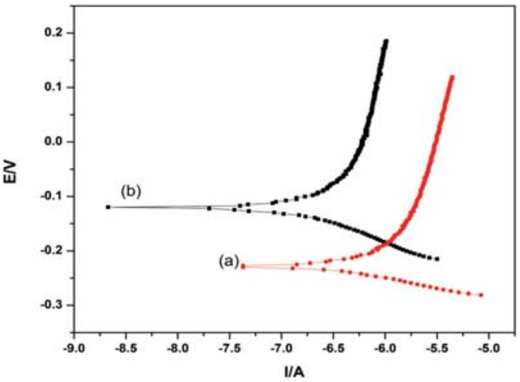

Fig.6 Potentiodynamic polarization analysis of a) Bare 316 L SS, b)TiN/TiAlN multilayers in SBF.

The corrosion current density of the multilayer and single layer coatings was found much lower than that of the bare substrate. The TiN/TiAlN multilayered coating has performed very well and showed superior corrosion resistance on the basis of corrosion current density and the corrosion potential. The corrosion resistance of TiAlN is better than TiN because addition of third element (such as Al) to the transition metal nitrides improves the corrosion resistance [16]. During the chemical attack Al easily forms an Al_2O_3 layer on the surface of the coating, which passivates the surface and prevents further corrosion attack [17]. The presence of a passive layer leads to an additional resistance to the corrosive medium passing through the pores.

4. Conclusion

Multilayer coatings of TiN/TiAlN were deposited on Si wafer and 316L stainless steel substrate substrates by plasma ion beam sputtering technique to improve the corrosion resistance. X-ray diffraction analysis exhibited FCC crystal structure. XPS spectra exhibit the characteristic peaks of Ti2p, Al 2p, N1s and Cls at the corresponding binding energy. The uniform surface morphology with columnar structure was observed from the AFM and HRTEM images. A maximum hardness of 30 GPa was observed for TiN/TiAlN coatings. The superior corrosion resistance in SBF was noticed for the multilayer coated specimen exhibiting its suitability for implant applications.

Acknowledgement

One of the authors (B.S) thanks the Japan Society for the Promotion of Science, Japan for the award of FY 2011 JSPS Long term Invitation fellowship.

References

1) M. Long, HJ. Rack, *Biomaterials*, **19** (1998) 1621.
2) P. Klementa, Y.J. Dua, L. Berrya, M. Andrewa, A.K.C. Chan, *Biomaterials*, **23** (2002) 527.
3) M. Long, HJ. Rack, *Biomaterials*, **19** (1998) 1621.
4) M.T. Raimondi, R. Pietrabissa, *Biomaterials,* **21** (2000) 907.
5) S.J. Bull, A.M. Jones, *Surf. Coat. Technol.,* **78** (1996) 173.
6) A.A. Voevodin, J.M. Schneider, C. Rebholz, A. Matthews, *Tribol. Int.,* **29** (1996) 559.
7) H. W. Wang, M. M. Stack, S. B. Lyon, P. Hovsepian, W. -D. Münz, *Surf. Coat. Technol.,* **135**, (2000) 82.
8) W.D. Sproul, *Surf. Coat. Technol*., **86/87** (1996) 170.
9) D. V. Shtansky, N. A. Gloushankova, I. A. Bashkova, M. I. Petrzhik, A. N. Sheveiko, Ph. V. Kiryukhantsev-Korneev, I.V. Reshetov, A.S. Grigoryan and E.A. Levashov, *Surf. Coat. Technol.*, **201** (2006) 4111.
10) P.B.Mirkarimi, S.A.Barnett, K.M.Hubbard, T.R. Jervis, and L.Hultman, *J. Mater. Res.*, **9** (1994) 1456
11) B.D. Cullites, Elements of X-ray Diffraction, Addison-Wesley, Ready, MA, 1972.
12) L. Rosenberger, R. Baird, F. McCullen, G. Auner, G. Shreve,. *Surface and Interface Analysis*, **40** (2008)1254.
13) JF. Marco, JR. Gancedo, MA. Auger, O. Sanchez, JM. Albella, *Surface and Interface Analysis*, **37** (2005) 1082.
14) AC. Agudelo, JR. Gancedo, JF. Marco, D. Hanzel, *J. Vac.Sci and Tech A*., **15** (1997) 3163.
15) M. Balaceanu, M. Braic, D. Macovei, MJ. Genet, A. Manea, D. Pantelica, V. Braic, F. Negoita, Journal of Optoelectronics and *Advanced Materials*, **4** (2002)107
16) H. Alanyani, RM. Souto, *Corrosion*,**59** (2003) 851.
17) L. Cunha, M. Andritschky, L. Rebouta, K. Pischow, *Surf. Coat. Tech.* **116** (199)1152.