# ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY OF COMPLEX TITANIUM NITRIDE COATING WITH THIN SURFACE OXIDE FILM DEPOSITED ON PURE TITANIUM

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An approach to surface modification for direct formation of nanosized anatase over cathodic arc PVD deposited (Ti,AI,V)N coating at a temperature of about 150 °C is proposed. In order to determine the surface structure influence on the electrochemical properties, bare and coated samples were exposed to Ringer-Braun physiological solution. The aim was to compare their corrosion performance (impedance characteristics, obtained by means of EIS and cyclic voltammetry (CV)) during immersing over an extended period of time - 2 hours, 1 and 7-days while the average temperature was close to the human body level (37±1°C). The capacitive behavior of the coated sample indicates a phase angle close to 71° and slightly decreasing impedance modulus /Z/ because of disruption by the high initial hydration and ions diffusion from the saline. The corrosion resistance of the coated system decreases as a function of time as a result of the thin oxide dissolution and lack of repassivation of the nitride. The characterization of the surface layer of the coating was obtained by scanning electron microscopy (SEM), glow discharge optical emission spectrometry (GDOES), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) analysis of core electron levels.

Keywords: biomaterials, nanostructures, metallic materials, materials research, PVD coating

#### 1. Introduction

In order to improve the osseointegration process, the implant surface needs to undergo morphological and physicochemical modification. In fact, there is evidence that the unique properties of titanium oxide could lead to different biological responses at several levels, including biomolecular interactions, cellular behavior, tissue response and biomechanical stability [1]. As the cell-surface interaction takes place over a few atomic distances, compositional modification at atomic level on the implant surface could influence the biocompatibility and osseointegration prognosis in vivo [2].

The excellent biocompatibility of TiO<sub>2</sub> has been proven by many authors [3-7]. The nanocrystal phases have large surface to volume ratio that facilitates the interaction between the coating and bioactive proteins and cells. On the other hand, the stability of the oxide and diffusion processes in the electrochemical system depend strongly on the composition, atomic structure, boundary conditions, oxide integrity, and thickness of the film that chemical strongly correlates with the and mechanical stability of the implants, especially when it is known that reduction in grain size caused a deleterious effect on the corrosion resistance.

Except for the high resistance to corrosion, an additional requirement for the surface up-scaling modification for hard tissue implants is to provide a highly reliable mechanical support of the bone implant itself and the growing tissue. A good opportunity that responds to that requirement is the deposition of a hard and durable TiN film. Some studies concerning oxidation of TiN coating that serves different purposes in a variety of the nitride applications are reported [8-14]. Because of the oxidation resistance of TiN, the large majority of investigations are carried out at temperatures exceeding 400°C [8-11] either at low pressure [12-14] in air and oxygen or at atmospheric air conditions and only a few at room temperature [12], where no  $TiO_2$  is formed. Even at high temperatures, the slower oxidation rate allows oxide thickness of the nitride samples to be effectively controlled simultaneously with ensuring satisfactory bonding strength with the oxide [13].

Despite the evidence for TiN suitability for medical application [15, 16], the biocompatibility of TiO<sub>2</sub> is more pronounced – it has bioactive properties and additionally prevents diffusion of toxic metal ions into the body. Furthermore, the oxidation process of the surface would ensure better fatigue durability of the hard coating only if

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Chemical composition (wt. %) of the substrate and target materials

Element		v	Fo	Mp	60	<b>Cr</b>	Мо	Dd	Nb	Цf	ті
Material	A	v	re	IVIII	00		WO	Fu		п	
Substrate	0.19	0.17	0.02	0.02	0.08	0.09	0.22	-	0.33	0.13	Bal.
Target	5.21	4.40	0.14	0.11	0.06	-	0.17	0.15	0.36	0.04	Bal.

the TiO<sub>2</sub> layer is thin enough [17]. In the present study, time and low temperature controlled vacuum glow discharge oxidation of arc-PVD deposited (Ti,AI,V)N coating is applied for the purpose of having a compositional gradient: (Ti,AI,V)N $\rightarrow$ TiO<sub>2</sub>. The glow discharge oxidation appears practically useful since one chamber allows carrying out both deposition and post-oxidation treatment in a single technological operation, simply varying the bias value, reactive gases, working pressure, and temperature.

The excellent resistance to corrosion and high stability of pure Ti in physiological solutions is well known from literature [18, 19]. For comparative electrochemical impedance purposes, spectroscopy (EIS) is carried out for pure Ti and (Ti,AI,V)N/TiO<sub>2</sub> coating titanium in external conditions reproducing as near as possible those in the body. The (Ti,Al,V)N/TiO<sub>2</sub> coating morphology, crystallinity, and composition estimated by different analysis - SEM, XRD, GDOES and XPS with selective excitation energies around the Ti 2p, O 1s and N 1s orbitals are used to explain the electrochemical behavior of the coating.

#### 2. Material and methods

#### 2.1. Samples and coating preparation

The chemical compositions of bare Ti and target material used for the experiment, determined by JEOL JXCA-733 Microprobe scanning electron microscope (SEM) equipped with wavelength dispersive spectrometers (WDS), were shown in Table 1.

Specimens in disk form (Ø20×6 mm) of commercially pure Ti (cpTi) were prepared by grounding using SiC paper before fine-polishing. For easing microstructure and XPS analysis, together with Ti samples rectangular (10×20×0.1 mm) tantalum foils and ceramic plates were also coated. All of the samples were ultrasonically washed with absolute ethanol, acetone, isopropanol, rinsed with distilled water for 5 min and dried.

For the (Ti,Al,V)N/TiO<sub>2</sub> coating deposition, a hand-made semi-industrial installation for cathode arc deposition TITAN 1-4 was used. The evaporating system in the cubic vacuum chamber with water-cooled walls was positioned on the sidewall. The samples were hanged near the center of a clockwise-rotating with a frequency of 0.5 Hz turntable. First, a cleaning in glow discharge (substrate bias -400V) was applied in pure Ar atmosphere at a pressure of 2.5.10<sup>-2</sup> mbar for 60 min. To ensure coating stress relaxation and

necessary adhesion, a very thin pure layer from the target (at  $2.5.10^{-3}$  mbar for 5 min.) was then applied. The (Ti,Al,V)N film was made by reactive arc deposition in the N<sub>2</sub> atmosphere at 300°C substrate temperature for a time of 120 min., 120 A arc current (3000 W target power), bias -250 V and 2.5.10<sup>-3</sup> mbar pressure in the working chamber. Directly after deposition, on the (TiAlV)N layer a second TiO<sub>2</sub> film was made by oxidizing, using glow discharge at a bias voltage of 400 V in a dry oxygen atmosphere at a pressure of  $2.5.10^{-2}$ mbar for a deposition time of 90 min. There was no vacuum break in between the cleaning, deposition, and vacuum oxidation.

### 2.2. Surface analysis techniques

The cross-sectional fractured images were taken from the mechanically bent and twisted foil samples in which some parts of the coating had fragmented. been cracked and Surface morphology tests of the samples were carried out by using SEM JEOL JSM-5510 and accelerating beam voltage of 10 kV. Prior to the analysis, each sample was coated with a thin layer of gold. The surface chemistry of the samples was investigated by using SEM - LYRA I XMU, Tescan equipped with energy dispersive spectrometer (EDS Quantax 200, Bruker) under an accelerating beam voltage of 20 kV. The chemical profile composition (varying from the outermost surface towards the substrate) of the coating was evaluated by Glow Discharge Optical Emission Spectrometry (GDOES), by using LECO instruments GDS-750 QDP apparatus. The tested surface area of the samples was approximately 12.56 mm<sup>2</sup>.

The bare substrate and coating were characterized by X-ray diffraction analysis by using URD6 Seiferd&Co diffractometer with CuK $\alpha$  radiation, operating at 40 kV and 30 mA in the angle range of 20°-80° with 0.1° step and counting time of 10s per step. Experiments were conducted in symmetrical Bragg-Brentano (B-B) and glancing angle X-ray diffraction (GAXRD) mode. Glancing angles of 3° were used for the coated sample. The diffraction patterns for each compound were analyzed by Match!3 software.

XPS measurements were carried out in the analysis chamber of the electron spectrometer ESCALAB-MkII (VG Scientific) with a base pressure of 2.10<sup>-10</sup> mbar. The spectra were excited with Mg-K $\alpha$  ( $h\nu$  = 1253.6 eV) radiation. The sample surface was not charged during spectra acquisition, so no charge corrections were made. O 1s, Ti 2p, and N 1s photoelectron lines were recorded at 90° and 20° incidence angle with

Table 1

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respect to the surface. In order to facilitate interpretation of data of the delocalized N 1s spectra some samples were heated in hot air up to  $\sim 600^{\circ}$ C and after that cooled in air.

Before electrochemical tests, the polished bare Ti and coated samples were cleaned in nonionic detergent, rinsed in deionized water and after that in NH<sub>4</sub>OH: H<sub>2</sub>O<sub>2</sub>: dH<sub>2</sub>O solution mixed in 1:1:5 ratio for 1 minute, washed with deionized water, and dried. Corrosion measurements were performed VoltaLab in 10 а Potentiostat/Galvanostat system with reference Ag/AgCI and auxiliary platinum electrode, provided with Voltamaster 4 software at open circuit potential (OCP). Bare Ti and coated specimens with the exposed surface of 1 cm<sup>2</sup> were used as working electrodes. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were obtained at Ringer-Braun's solution (infusion bank containing 8.60 g/L NaCl, 0.30 g/L KCl, 0.33 g/L CaCl<sub>2</sub>.2H<sub>2</sub>O) at 37±1 °C and naturally aerated conditions. The pH of the solution equalled to 5.70±0.02 at 37°C and was measured by using a portable HI 8424 pH meter. As known, organic residues on the substrate surface could contribute to a faradaic current, which decreased the charge transfer resistance and polarized the electrode, that kind of solution (not in proteincontaining serum) was used in order to make external conditions more severe. Five CV cycles for each sample after 2, 24 and 168 hours of immersion at a scan rate of 10 and 100 mV/min was performed on each sample under potential condition varying from -500 mV to 1000 mV. After galvanostatic cycling, the EIS was performed with excitation amplitudes of 10 mV vs OCP from 0.1 Hz to 100 kHz on a regular basis with increasing exposure time in saline. Intact coating capacitance Cc was determined from impedance modulus /Z/ at 10 kHz by the equation (1) [20]:

$$C_{c} = \frac{1}{2\pi . 10^{4} |Z|_{10 \text{kHz}}}$$
 (1)

Volume fraction of water ( $VF_{H2O}$ ) was estimated according to the formula (2) [21]:

$$VF_{H_{2}O} = \frac{\log c_t / c_0}{\log \varepsilon_w}$$

where  $c_t$  is coating capacitance at time t;  $c_0$  is the initial coating capacitance, and  $\varepsilon_w$  is the dielectric constant of water. Surface corrosion failure after immersion was investigated by using optical microscopy at normal and polarized light regimes.

(2)

#### 3. Results

As seen in both Fig. 1 A and B, the droplet (macro- and microparticles) phase that increased the surface roughness and was formed because of the high cathode power was an integral part of the complex coating. There was a pronounced columnar fiber-like growth of the nitride grains (Fig. 1 B) which is typical for that kind of PVD coating. The single crystal columns were separated from one another by tight and well-defined grain boundaries. A thin oxide layer covering and partially entering in the columnar grains and along the grain boundaries was observed (Fig. 1 B). The fine polycrystalline structure of the TiO<sub>2</sub> film over the nitride coating is presented in Fig. 1 C and D. The whole coating thickness was about 2.8–3 µm.

XRD measurements identified the crystal phases reflected from the bare substrate ( $\alpha$ -Ti) and those refracted from the coating (Fig. 2). The coating XRD pattern reveals that the nitride was strongly textured and constituted basically by (220) textured (Ti,AI,V)N grains. Small (111) and (200) reflections were also noticed in the Bragg-Brentano pattern. As the diffraction pattern peak intensity of TiO<sub>2</sub> increases with increasing particle



Fig. 1 - SEM images at different resolutions and different tilted angles ( $\theta$ ) of the untreated (Ti,AI,V)/TiO<sub>2</sub> coating: (A) ruptured coating,  $\dot{\theta} = 45^{\circ}$ ; (B) a medium scale image of the cross-section coating morphology ( $\theta = 45^{\circ}$ ) showing the intermediate layer with columnar growth structure and the lighter looking surface oxides; (C) a further enlarged and rotated image ( $\theta = 90^\circ$ ) corresponding to the nano-sized oxide located at the coating surface; (D) nanostructure of the surface oxide ( $\theta = 90^{\circ}$ ).

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size [22], the registered low-intensity peaks could be attributed to the small oxide thickness and ultrafine grain size compared to the nitride. The small (101) reflection of anatase phase appeared only in GAXRD pattern together with more intense (111), (200), (311) and (222) reflections of TiN without giving rise to (220) peak of the nitride.

In the light of GDOES results, shown in Fig. 3 A, lower Ti and especially AI and V concentration was found at the oxidized surface of (Ti,AI,V)N layer. The increase in Ti and N content corresponded to a decrease in the oxygen profile line. The lack of steeper concentration stages was due to the increased surface roughness (seen microscopically) and the difference in the thickness and penetration depth of the oxide film into the (Ti,Al,V)N. Despite the difficulties arising from the diffuse nature of oxide-nitride interfaces, the coating surface could be divided into several zones. It is important to note that the oxide layer at the surface was thin and reached up to 20 nm in depth. After that, the oxygen concentration sloped down to over 50 nm where titanium oxynitrides (TiN<sub>x</sub>O<sub>y</sub>) with variable concentration of O and Ti and predominance of N were formed. The concentration of the dissolved oxygen in the nitride continued to decrease and stayed at a level of 5 - 4 at. % beyond 500 nm depth. At the same time, nitrogen concentration increased towards the surface, reached up about 60 at. % and slowly decreased to ~ 55 - 56 at. % in depth of (Ti,AI,V)N.

Elemental analysis of the prepared TiO<sub>2</sub> film was also performed by EDX spectroscopy (Fig. 3 B). Besides major K<sub>a</sub>-Ti and K<sub>a</sub>-O peaks, additional peaks attributed to small quantities of Al, V, and N were observed. EDX spectra revealed the presence of Ti and O in the thin surface layer and thus formation of TiO<sub>2</sub> thin layer was confirmed. The exact ratio of Ti:O is hard to be determined because the film is too thin and a part of the signals could come from the underneath oxynitride/nitride layer.

Narrow scans of the electronic energetic distribution of Ti 2p, O 1s, and N 1s orbitals (Fig. 4) revealed that in the spectra of titanium chemical states (Fig. 4 A), 2p<sub>3/2</sub> (458 eV) and 2p<sub>1/2</sub> (464 eV) spin-orbitals were split in two and the higher signal belongs to the 2p<sub>3/2</sub> orbital. The peak at 458.7 eV indicated the Ti4+ state in stoichiometric TiO2 where Ti was surrounded by oxygen atoms (O<sub>2</sub>-Ti-O<sub>2</sub>) as it was found in the majority of titanium oxides [23]. The 2p<sub>3/2</sub> peak shift towards low energy was detected at normal emission, which indicated a reduction of Ti4+ in the stoichiometric TiO2 state towards Ti<sup>3+</sup> (as in Ti<sub>2</sub>O<sub>3</sub> and TiN<sub>x</sub>O<sub>y</sub>), a decrease of the coordination number of Ti and a larger concentration of oxygen vacancies. The widening of the photoelectron spectra at 90° confirmed the increase of oxidation states of Ti in depth. The O 1s peak (Fig. 4 B) that appeared at 530 eV was attributed to signal of oxygen in the crystalline TiO<sub>2</sub>



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Fig. 2 - XRD pattern of the bare Ti and (Ti,Al,V)N/TiO<sub>2</sub> coating as deposited on the substrate. A comparison of the bare Ti and coated pattern obtained in GAXRD at 20-34° is shown on a small scale.



Fig. 3 - Elements depth profile (A) of the surface area of the (Ti,AI,V)N/TiO<sub>2</sub> coating and EDX spectra (B) of the surface TiO<sub>2</sub> thin film after synthesis.



Fig. 4 - Quantification regions of photoelectron line of Mg-Kα excited: (A) Ti 2p; (B) O 1s; (C) air heated N 1s core level peaks obtained on the surface of (Ti,AI,V)N/TiO<sub>2</sub> coating



Fig. 5 - CV voltammograms of: (A) bare Ti sample at 10 mV/s; (B) and 100 mV/s; (C) coated sample at 10 mV/s; (D) coated sample at 100 mV/s scan rate. All the experiments are held in Ringer-Braun solution at 37° C, pH 5.7.

lattice. The greater area belonged to O 1s O<sup>2-</sup> peak, which could be assigned to Ti-O-Ti and O<sub>2</sub>-Ti-O<sub>2</sub> as well as C-O-Ti chemical states that could be a part of the organometallic surface. The O 1s HBE peak (Fig. 4 B) that decreased in depth had been ascribed to non-stoichiometry of the oxide or hydroxyl groups (-OH) adsorbed or chemically bound to the surface cations [24].

At the untreated coating surface, nitrogen had small participation (N~1 wt. %) so that its weak signals could be confused with other overlapping peaks. In order to eliminate distortions, N 1s energetic states of the air heated and air-cooled samples are shown in Fig. 4 C. Near the surface the 400.3 eV peak (N 1s I) could be attributed to N-O bonding. The centered at ~ 402.86 – 402.97 eV peak at normal Mg-K $\alpha$  emission revealed the presence of either N<sub>2</sub> gas molecules or replaced N atoms by the O [12] or vice versa that remained dissolved in the oxide/oxynitride.

For both bare and (Ti,Al,V)N/TiO<sub>2</sub> coated samples in the low voltage scans (Fig.5 A and C) where the diffusion layer grew farther from the electrode, the flux was small and the current was also lower as compared to the higher voltage scans (Fig. 5 B and D). At both scanning rates, the larger integrated area compared to that of the bare Ti suggests a lower capacitive response of the coated electrode. For the coated sample the difference between the voltammograms obtained at 10 and 100 mV/s scan rate was only the larger charging current observed at higher scan rate with no indication of peaks corresponding to charge-transfer processes.

Each set of five voltammograms of the bare Ti sample at 100 mV/s scan rate for 2 and 24 hours overlapped closer than that of 168 hours (Fig. 5 B). In contrast to CV curves after 2 hours, the diffusion-controlled oxidation of the electrode was clearly seen after soaking time of 168 hours because of the distinct anodic peak currents shifted to higher potentials upon repeated scans. In comparison, the voltammograms of (Ti,AI,V)N/TiO<sub>2</sub> shown in Fig. 5 C and D, did not display sharp redox peak currents. The reduction of some titanium ions near the surface could trigger electronic conductivity leading to higher currents at low potentials. At higher potentials, the positive sweep of the current was smaller because of the small oxidation contribution.

For bare Ti after 2 and 24 hours of immersion, the Bode - phase angle vs. frequency plot (Fig. 6 A) showed only one time constant and high capacitive response which had typical passive-transpassive behavior and was identified by other authors [25]. The phase angle close to -90° indicated a near-capacitive impedance. After 168 hours Ti remained passive and the change in the phase angle indicated interaction of two-time constants - of kinetic electrochemical and diffusion mechanism [26] associated with the formation of duplex oxide layer - porous and compact one. The shoulder at low frequency (LF) for 168 hours of immersion suggested the passive layer response during the electrochemical process connected with the penetration of the electrolyte through the intrinsic defects in the oxide layer. The maximum values of the phase shift angles of the coated sample in a wide range of frequencies (Fig. 6 A) reached approximately  $\theta \sim 71^\circ$  with increasing linear portion at low and first half of intermediate frequencies after 168 hours of immersion. That lower phase angle indicates that the oxide film is thin, porous and less protective. The linear region of log /Z/ vs. log f curve with slope lower than 1 indicated diffusion process that took place through the single thin oxide layer. The higher slope of bare Ti after 168 hours of immersion denoted high barrier layer capacitance while the lower /Z/ value at HF was related to the presence of more porous outer layer [27].

The impedance value of bare substrate on Nyquist plot (Fig. 6 C) was higher than those of the coated material in all time periods. The greater

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Fig. 6 - Plots of bare and coated Ti: (A) Bode plot of impedance modulus vs. frequency; (B) phase angle vs. frequency; (C) Nyquist plot (the inset shows a zoomed view of the Nyquist plot at HF region) and (D) areal capacitance vs. frequency plot after 2, 24 and 168 hours of immersion in Ringer-Braun solution at 37°C, pH 5.7.

Table 2

Calculated parameters of the EIS measurements of the bare and  $(Ti,AI,V)N/TiO_2$  coating: t – immersion time;  $Z_{0.1Hz}$  – impedance value at 0.1 Hz;  $R_s$  – uncompensated (electrolyte) resistance,  $C_c$  – intact coating capacitance;  $VF_{H20}$  – volume fraction of water.

Sample	t, h	$Z_{0.1Hz}, k\Omega.cm^2$	$R_s, \Omega.cm^2$	C <sub>c</sub> , µFcm⁻²	<b>VF</b> <sub>H20</sub>	
	2	0.85	5.39	88.09	2.459	
Bare	24	1.15	5.18	83.17	2.446	
	168	4.97	5.29	85.09	2.451	
Control	2	0.9	11.16	180.58	2.623	
Ti	24	0.88	7.74	126.94	2.543	
	168	0.63	3.30	54.02	2.348	



Fig. 7 Micrographs of samples' surface after the 7-day test of immersion: bare Ti surface image acquired with normal (A) polarized and light regime (B); coated Ti image acquired with normal (C) and polarized light regime (D).

semi-circle diameters of the bare Ti indicated, the better-protecting properties of the oxide film. The almost ideal straight lines along the imaginary axis for 2 and 24 hours immersed bare Ti samples at LF suggested that the electrode had low diffusion resistance [28] and pure capacitive behavior. As the radius of the capacitive loop decreased with the increase of time, the impedance decreased sharper confirming the results shown in Fig. 6 B. Therefore, for bare substrate, passivity of the

surface film was gradually increased with time. For coated samples the small semicircles in the HF region reflecting the charge-transfer process were followed by straight inclined lines at LF region showing that corrosion rate was limited by slow open boundary finite length diffusion of solution particles through the passive film and coating's defects (Fig. 6 C). Charge-transfer resistance (Rct) decreased with the increase of time while the 168hours immerse coated sample showed the fastest diffusion. Plotting capacitance vs. frequency (Fig. 6 D), it could be seen that as opposed to bare substrate coating capacitance increase with time of immersion and had higher values at low and medium frequency range. Higher capacitance values indicated that the surface film was more exposed to pitting corrosion. At HF, different resistance effects dominated over capacitive impedance. The calculated parameters from the EIS measurements are summarized in Table 2.

The micrographs of the surface of the bare and coated Ti after 168 hours of immersion shown in Fig. 7 revealed the pitting morphology of both samples. The re-passivation of bare Ti darkened the surface (Fig. 7 A) of the material in which some larger pits were revealed (Fig. 7 B). The localized attacks causing larger, as well as small pits on the coated surface, were also clearly seen in Fig. 7 C and D.

## 4. Discussions

The electrochemical response at HF is related to the differences in pore morphology within the micro-defects, droplets of the film, and solution resistance. The increase in roughness offers a large number of peaks and grooves that reduce pitting corrosion resistance. The droplets that pass the whole thickness of the coating are known to initiate galvanic and crevice corrosion between defect and substrate because of permitting solution along the sidewall down to substrate [29]. The covering oxide contributes to partial closing of the pores and voids of the heterostructured coating. The heavy ion bombardment of particles with high energies causes densification and therefore less intercolumnar voids in the microstructure of nitride (Fig. 1) because of the enhanced adatom mobility, but the areas around the droplets are highly defective and corrosion sensitive. The applied high bias voltage also increases the deposition temperature that together with the dominating metal ion flux result in enhanced surface diffusivity of adatoms and preferred orientation of the growing film [30]. Therefore, both bias deposition and higher power density cause preferential growth along the (220) crystal plane that has lower planar density than (111) and (200) and, therefore, greater surface energy.

In contrast, oxygen is well-known for its high reactivity and thus it incorporates in existing

structures of (Ti,Al,V)N occupying some of the positions of nitrogen atoms or defects in the fcc (Ti,Al,V)N lattice. The lateral diffusion of O in the (Ti,Al,V)N coating evolves slowly because of the low-temperature value, presence of AI that improves oxidation resistance [31], and limited quantity of crevices and microvoids in the initially nitride. deposited Therefore. as oxygen concentration increases. nitride-oxide transformation undergoes the following reaction:  $TiN_x + \frac{1}{2}O_2 \rightarrow TiN_xO$ (4)

The inward oxidation initially forms intermediate TiNxOy phases of substitutional nature. The over-stoichiometric composition of nitride near the surface (Fig. 3) favors N2 gas formation caused by O invasion in the octagonal vacancies and/or partial replacement of nitrogen atoms that triggers their recombination, thus decreasing the binding energy of the crystallites and causing additional coating micro-defects. The nitrogen-rich regions go through a phase transformation and oxynitride is likely to be additionally oxidized by the following reactions:  $2\text{TiN}_x\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{Ti}_2\text{O}_3 + x\text{N}_2$ (5) $Ti_2O_3 + \frac{1}{2}O_2 \rightarrow 2TiO_2$ (6)

Through post-oxidation, columnar densely packed nitride crystallites are replaced by small grains with expanded tetragonal spacing. The negative pressure [32], low temperature and low concentration of ionic species with low energy favor the anatase to be more stable than rutile in the particular oxidation conditions. As a consequence, oxygen diffusion triggers a change in nitride texture near the surface (Fig. 2).

For the coated sample superior electrical potentials are observed with higher value of current response and CV area. That is largely contributed to an increased true surface area of the nanocrystalline structure and consequent changes in the diffusion limit of the electrolyte ions at higher scan rates. Additional current peaks due to the presence of AI and V in the coating are not observed suggesting that they are randomly located within the coating without forming any AI or V- rich areas. The increased potentials in negative direction imply lack of film formation and dissolution of oxide particles while larger area of the hysteresis loop after 168 hours of immersion demonstrates a higher rate of pits formation. The decrease of impedance with exposure time on the Nyquist plot at LF for the coated sample indicates high interface activity and increased corrosion rate. As impedance response is very much dependent on the film thickness, the diffusional impedance occurring at HF causes Nyquist plot to appear like a single semicircle decreasing with the time of immersion and straight diffusion tail. The higher slope than 45° at HF (the pure Warburg line) V. Panella at al. [33] explains with the waiting of the diffusion species after each jump for a period

because of sticking in the diffusion path but that behavior is also typical for a porous system with capacitive walls.

The maximum broadening of the coated sample in the Bode phase plot indicates presence of two interfaces - electrolyte-coating and coatingsubstrate. As coating capacitance (C<sub>c</sub>) evaluates the electrolyte inward invasion, the coated sample undergoes a strong initial saline uptake. After 2 and 24 hours, the Cc is high because the nanostructured surface oxides/oxynitrides with expanded tetragonal spacing, higher roughness, many grain boundaries, pinholes, and droplets incorporate high water content leading to higher dielectric strength and volume fracture of water. Simultaneously, diffusing particles (dissolved oxygen and chloride ions) from the solution are trapped in these small spaces and spent more time to diffuse through the film towards the interface. The reciprocal capacitance of the passive film is proportional to the film thickness and it is obvious that the oxide film deposited on the nitride coating is deteriorating with time. Rs lowering at day 7 confirms not only the slow uniform dissolution of the thin oxide, but also the increase of the electrical conductivity of the coated sample. The electrochemical reduction of oxide functional groups provides a drop off in R<sub>ct</sub> values which reveals that R<sub>ct</sub> and double layer capacitance are very small. With the immersion, Cc and VFH20 values decrease which could also be attributed to the denser nitride structure, good coating adhesion or filling of the pores with corrosion products. However, saline inward diffusion through pin-holes or micropores of the nitride with depleted oxide film increases the electrochemical activity at the metal/electrolyte interface and diffusion rate so that solution particles accelerate local pitting corrosion. Conversely, the immersed bare substrate maintains almost the same level of C<sub>c</sub> probably because of small oxide thickness. The natural metal oxides are claimed to be amorphous and stoichiometrically defective [34] or rutile containing [35] with a thickness of 3-10 nm [36]. According to B. Sivakumar et al. [37], pure Ti forms an extremely impermeable TiO2 film in chloride containing solution with higher protection ability. The thin (Ti,Al,V) film, deposited on Ti substrate as an intermediate layer is known to be more susceptible to corrosion than pure Ti [38] especially when it is nano in size. In contrast to the repassivation of pure Ti related to hydrolysis of titanium chloride forming thicker TiO2 passive film [18], oxide formation do not take place on the PVD (TI,AI,V)N surface because of the higher oxidation resistance and inert character of the nitride [39].

## 5. Conclusions

The combined surface treatment for titanium materials proposed in the study gives the

opportunity of achieving consistent nanostructured oxide on the (Ti,Al,V)N surface. As the samples are being negatively biased during vacuum oxidation, the low deposition temperature and low pressure provide the necessary mobility for complete surface phase segregation and oxidation to thin tetravalent TiO<sub>2</sub> without oversaturation with oxygen. However, EIS and XPS results evidence the presence of defects in the coating. Although nitride is comparatively thick and dense, the surface nanostructured oxide appears to facilitate rather than impede corrosion reactions. The mechanism of oxidation follows inward oxygen diffusion in the over stoichiometric nitride. Comparing the results with pure Ti, it seems that the examined (Ti,AI,V)N/TiO<sub>2</sub> coating on Ti substrate shows electrochemical worse performance in aggressive biological environment. With the elapsed time of immersion, the oxide layer within the coating is not likely to recover in the chlorine-electrolyte solution. The coated sample demonstrates unstable surface impedance properties in Ringer-Braun solution which is extremely aggressive as compared to what is supposed to occur in human body. The electrochemical behavior of the coating is largely influenced by the defects in the cathodic arc plasma deposited (Ti,Al,V)N compared to the effect of the obtained surface nanostructured oxide which effect is only temporary but determinative for the coating hydration. However, the small defects of the coating do not grow significantly with immersion time because of the passive substrate and good coating-substrate adhesion.

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#### REFERENCES

- J. Lausmaa Surface spectroscopic characterization of titanium implant materials. J. of Electron Spectrosc. Relat. Phenom. 1996, 81(3), 343 <u>http://dx.doi.org/10.1016/0368-</u> 2048(95)02530-81.
- E. Wróbel, M. Witkowska-Zimny, J. Przybylski, Biological mechanisms of implant osseointegration. Ortopedia Traumatologia Rehabilitacja 2010, **12**(5), 401.
- A. Majeed, J. He, L. Jiao, X. Zhong, Z. Sheng, Surface properties and biocompatibility of nanostructured TiO<sub>2</sub> film deposited by RF magnetron sputtering, Nanoscale Res. Lett. 2015, **10**(56), 1.
- Lett. 2015, 10(56), 1.
  M.-Y. Lan, C.-P. Liu, H.-H. Huang, S.-W. Lee, Both Enhanced Biocompatibility and Antibacterial Activity in Ag-Decorated TiO<sub>2</sub> Nanotubes, PloS One 2013, 8(10), e75364; <u>https://doi.org/10.1371/journal.pone.0075364</u>.

- Y. Wang, C. Wen, P. Hodgson, Y. Li, Biocompatibility of TiO<sub>2</sub> nanotubes with different topographies, J. of Biomedical Materials Res. Part A, 2014, **102**(3), 743.
- J. E. Park, S. Park, T. S. Bae, M. H. Lee, Electrophoretic deposition of carbon nanotubes over TiO<sub>2</sub> nanotubes: Evaluation of surface properties and biocompatibility, Bioinorg Chem Appl. 2014, 236521. doi: 10.1155/2014/236521.
- M. Li, G. Huang, Y. Qiao, J. Wang, Z. Liu, X. Liu, Y. Mei, Biocompatible and freestanding anatase TiO<sub>2</sub> nanomembrane with enhanced photocatalytic performance, Nanotechnology 2013; **24**(30), 305706, doi:10.1088/0957-4484/24/30/305706.
- J. Desmaison, P. Lefort, M. Billy, Oxidation of titanium nitride in oxygen: Behavior of TiN<sub>0.83</sub> and TiN<sub>0.79</sub> plates. Oxidation of Metals 1979,**13**(3), 203.
- F.-H. Lu, H.-Y. Chen, XPS analyses of TiN films on Cu substrates after annealing in the controlled atmosphere, Thin Solid Films 1999, 355-356, 374.
- H. Van Bui, A. W. Groenland, A. A. I. Aarnink, R. A. M. Wolters, J. Schmitz, A.Y. Kovalgin, Growth kinetics and oxidation mechanism of ALD TiN thin films monitored by in situ spectroscopic ellipsometry, Journal of The Electrochemical Society 2011, **158**(3), H214.
- L. Soriano, M. Abbate, H. Pen, M. T. Czyiyk, J. C. Fuggle, The interaction of N with Ti and the oxidation of TiN studied by soft X-ray absorption spectroscopy, J. Electron Spectrosc. Relat. Phenom 1993, 62, 197.
- P. Prieto, R. E. Kirby, X-ray photoelectron spectroscopy study of the difference between reactively evaporated and direct sputter-deposited TiN films and their oxidation properties, J. Vac. Sci. Tech 1995, A13, 2819.
- Y. Oshida, A. Hashem, Titanium-porcelain system. Part I: Oxidation kinetics of nitrided pure titanium, simulated to porcelain firing process, J. BioMed. Mater. Eng. 1993, 3, 185.
- Y. Oshida, L. W. Fung, S. C. Ishikbay, Titanium-porcelain system. Part II: Bond strength of fired porcelain on nitrided pure titanium, J. BioMed. Mater. Eng. 1997, 7, 13.
- A. P. Serro, C. Completo, R. o Colac, F. dos Santos, C. L. da Silva, J. M. S. Cabral, H. Araujo, E. Pires, B.Saramago, Comparative study of titanium nitrides, TiN, TiNbN and TiCN, as coatings for biomedical applications, Surf. Coat. Technol. 2009, 203, 3701.
- Y. Tamura, A. Yokoyama, F. Watari, T. Kawasaki, Surface properties and biocompatibility of nitrided titanium for abrasion resistant implant materials, Dent. Mater. J. 2002, 21, 355.
- D. Xie, H. Wang, R. Ganesan, Y. Leng, H. Sun, N. Huang, Fatigue durability and corrosion resistance of TiO<sub>2</sub> films on CoCrMo alloy under cyclic deformation, Surf. Coat. Technol. 2015, **275**, 252.
- J. E. G. Gonzalez, J. C. Mirza-Rosca, Study of the corrosion behavior of titanium and some of its alloys for biomedical and dental implant applications, Journal of Electroanalytical Chemistry 1999, **471**, 109.
- M. Aziz-Kerrzo, K. G. Conroy, A. M. Fenelon, S. T. Farrell, C. B. Breslin, Electrochemical studies on the stability and corrosion resistance of titanium-based implant materials, Biomaterials 2001, 22, 1531.
- M.-G. Olivier, M. Poelman, Use of electrochemical impedance spectroscopy (EIS) for the evaluation of electrocoatings performances, Recent Researches in Corrosion Evaluation and Protection, Prof. Reza Shoja Razavi (Ed.), ISBN: 978-953-307-920-2, InTech 2012, p.1.
- D. Loveday, P. Peterson, B. Rodgers, Evaluation of organic coatings with electrochemical impedance spectroscopy Part 2: Application of EIS to coatings, JCT Coatings Tech 2004, 88.

- K. Thamaphat, P. Limsuwan, B. Ngotawornchai, Phase characterization of TiO<sub>2</sub> powder by XRD and TEM, J. Nat. Sci. 2008, **42**, 357.
- Ma G. Olayo, F. González-Salgado, G. J. Cruz, L. Ma Gómez, G. García-Rosales, M. Gonzalez-Torres, O. G. Lopez-Gracia, Chemical structure of TiO organometallic particles obtained by plasma, Advancies in Nanoparticles 2013; 2, 229. <u>http://dx.doi.org/10.4236/anp.2013.23032</u>.
- A. Abidov, B. Allabergenov, J. Lee, H.-W. Jeon, S.-W. Jeong, S. Kim, X-ray photoelectron spectroscopy characterization of Fe doped TiO<sub>2</sub> photocatalyst, Int. J. Mater. Mech. Manuf. 2013, 1(3), 294.
- M. Basiaga, Z. Paszenda, W. Walke, Pł. Karasiński, J. Marciniak, Electrochemical Impedance Spectroscopy and Corrosion Resistance of SiO<sub>2</sub> Coated CpTi and Ti-6Al-7Nb Alloy Vol 4. Eds. Piętka E, Kawa J, Więcławek W., Springer 2014, **284**, 411.
- S. Luiz de Assis, S. Wolynec, I. Costa, Corrosion characterization of titanium alloys by electrochemical techniques. Electrochim. Acta 2006, **51**, 1815.
- I. Cvijović-Alagić, Z. Cvijović, J. Bajat, M. Rakin, Composition and processing effects on the electrochemical characteristics of biomedical titanium alloy, Corr. Sci. 2014, 83, 245.
- I. Shakir, M. Shahida, S. Cherevko, C.-H. Chung, D. J. Kanga, Ultrahigh-energy and stable supercapacitors based on intertwined porous MoO<sub>3</sub>–MWCNT nanocomposites, Electrochimica Acta 2011, **58**, 76.
- M. Fenker, M. Balzer, H. Kappl, Corrosion protection with hard coatings on steel: Past approaches and current research efforts, Surf. Coat. Techn 2014, 257, 182.
- Y. N. Kok, P. E. Hovsepian, Q. Luoa, D. B. Lewis, J. G. Wen, I. Petrov, Influence of the bias voltage on the structure and the tribological performance of nanoscale multilayer C/Cr PVD coatings, Thin Solid Films 2005, 475, 219.
- Y. Yin, L. Hang, S. Zhang, X. L. Bui, Thermal oxidation properties of titanium nitride and titanium–aluminum nitride materials - A perspective for high temperature air-stable solar selective absorber applications, Thin Solid Films 2007, **515**, 2829.
- D. A. H. Hanaor, C. C. Sorrell, Review of the anatase to rutile phase transformation, J. Mater Sci. 2011, 46, 855– 874.
- V. Panella, J. Krim, Adsorption isotherm study of the fractal scaling behavior of vapor-deposited silver films, Phys. Rev. E 1994, 49(5), 4179.
- D. A. Jones, Principles and Prevention of Corrosion. Macmillan Publishing Company 1995, 2<sup>nd</sup> Edn, Prentice Hall, New York.
- Y. Jun Lim, C. J. Andres, Surface Characterizations of Variously Treated Titanium Materials, The International Journal of Oral & Maxillofacial Implants 2001, 16(3), 333.
- K. G. Neoh, Hu X, Zheng D, Tang Kang E. Balancing osteoblast functions and bacterial adhesion on functionalized titanium surfaces. Biomaterials 2012, 33, 2813.
- B. Sivakumar, P. Lokesh Chandra, R.Singh, Role of surface roughness on corrosion and fretting corrosion behaviour of commercially pure titanium in Ringer's solution for bio-implant application, Applied Surface Science 2017, 401, 385.
- V. A. R. Barao, M. T. Mathew, W.G. Assuncao, J. Chia-Chun Yuan, M. A. Wimmer, C. Sukotjo, Stability of cp-Ti and Ti-6Al-4V alloy for dental implants as a function of saliva pH – an electrochemical study, Clin. Oral Impl. Res. 2012, 23, 1055.
- Y. Li, L. Qu, F. Wang, The electrochemical corrosion behavior of TiN and (Ti,Al)N coatings in acid and salt solution, Corr. Sci. 2003, 45, 1367.

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