

Article

Tailoring the Surface Performance of Near- β Ti-13Nb-13Zr Alloy Through TaN/Au Bilayer Coatings: Electrochemical Stability, Tribocorrosion Mechanisms and Biocompatibility

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Abstract

β -Type titanium alloys mitigate stress shielding through their low elastic modulus, but their limited wear resistance restricts their use in articulating surfaces. This study evaluated the effect of a 100 nm Au interlayer on the structural, electrochemical, tribocorrosion and biological behaviour of TaN coatings deposited by magnetron sputtering on aged Ti-13Nb-13Zr. Coatings were characterised by XRD, SEM and AFM and assessed by potentiodynamic polarisation, electrochemical impedance spectroscopy and ASTM G119 tribocorrosion tests in Ringer's lactate at 37 °C, ICP-MS, and MTT and LDH assays with MG-63 cells. Both coatings were columnar and dominated by δ -TaN; the interlayer attenuated the ϵ -TaN and γ -Ta₂N phases and increased the crystallite size from 24 ± 3 to 31 ± 2 nm. The TaN/Au system shifted the corrosion potential from -210 ± 18 to $+35 \pm 10$ mV vs. Ag/AgCl and lowered the corrosion current density 23-fold. Under tribocorrosion, the friction coefficient fell from 0.28 to 0.17, the wear volume fell 7.2-fold and the synergistic fraction fell from 35% to 14%. Ti release fell from 1.85 to 0.16 $\mu\text{g}\cdot\text{cm}^{-2}$ and 72 h cell viability rose from $82 \pm 5\%$ to $96 \pm 3\%$. A nanometric noble interlayer is therefore a promising strategy for articulating surfaces of β -titanium alloys.

Keywords: Ti-13Nb-13Zr alloy; tantalum nitride; gold interlayer; tribocorrosion; electrochemical impedance spectroscopy; biocompatibility



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1. Introduction

Metallic biomaterials for orthopaedic implants have evolved continuously with the aim of simultaneously improving their mechanical properties, chemical stability and biological response. Among them, titanium alloys have become established as one of the main options owing to their high specific strength, excellent corrosion resistance and adequate biocompatibility [1–6]. However, conventional alloys, and Ti-6Al-4V in particular, have an elastic modulus of about 110 GPa, far higher than that of cortical bone (10–30 GPa), which promotes the phenomenon known as stress shielding [7–9]. This mechanical mismatch alters the natural load distribution, promotes bone resorption around the implant, and may lead to premature loosening of the device. In addition, there are concerns about the

possible release of aluminium and vanadium, elements associated with adverse biological effects after prolonged implantation [2,8].

β -Titanium alloys stabilised with biocompatible elements such as Nb, Ta and Zr were developed to overcome these limitations [3,4]. Among them, the near- β Ti-13Nb-13Zr alloy has attracted growing interest because of its low elastic modulus, between 65 and 79 GPa depending on the microstructural condition [5,8], which reduces stress shielding and improves load transfer to the bone tissue. This alloy also offers high corrosion resistance, good formability and the absence of potentially cytotoxic elements [4,5]. These advantages, however, come with a significant drawback: its low hardness and wear resistance restrict its use in articulating components subjected to repetitive motion and high contact loads [10,11], a scenario in which wear and tribocorrosion are among the main causes of orthopaedic implant failure [12].

Tribocorrosion is not simply the sum of mechanical wear and electrochemical corrosion. On passive surfaces such as those of titanium, sliding contact continuously removes the protective oxide film and exposes bare metal to the electrolyte, which then repassivates at the expense of anodic charge [13,14]. This depassivation–repassivation cycle generates a synergistic term that may account for most of the material removed and is also directly responsible for the release of metallic particles and ions into the periprosthetic tissue [15,16]. Consequently, any surface protection strategy intended for articulating implants should be judged not only on its hardness or its corrosion resistance under static conditions, but on its ability to suppress this coupling.

A widely used strategy for increasing the surface durability of these alloys is the application of hard coatings produced by physical vapour deposition (PVD) [17,18]. In this context, coatings based on tantalum and its nitrides have shown particularly promising behaviour owing to their high hardness, chemical stability, wear resistance and good biocompatibility [19,20]. The stoichiometry of the nitride depends directly on the N_2/Ar ratio used during reactive sputtering, which promotes the successive formation of the γ -Ta₂N, ϵ -TaN and δ -TaN phases; these phases have a decisive influence on the hardness, adhesion and electrochemical behaviour of the system [21,22]. An excess of nitrogen, however, can lead to amorphous or over-stoichiometric structures that compromise corrosion resistance [23].

The main limitation of these coatings lies not in their chemistry but in their architecture. PVD nitride films usually grow with a columnar morphology, and the intercolumnar boundaries, pores and microdefects act as open channels through which the electrolyte reaches the metallic substrate, establishes a galvanic couple with a very large cathodic area and a very small anodic area, and triggers localised corrosion beneath the coating [24,25]. The practical consequence is well known: a ceramic coating may perform excellently in a short-term polarisation test and yet fail by delamination after prolonged immersion. Incorporating a metallic interlayer between the substrate and the ceramic layer is the classical answer to this problem, since it improves adhesion, relaxes residual deposition stresses, blocks the propagation of growth defects and adds a further barrier against corrosion; interlayers only 100 nm thick have been shown to be sufficient to suppress the effective porosity of multicomponent nitride coatings [26].

What distinguishes gold from conventional metallic interlayers Ti, Cr or Ni is its electrochemical nobility. A Ti or Cr interlayer protects through adhesion and defect sealing, but remains thermodynamically susceptible to dissolution once the electrolyte reaches it. Gold, by contrast, is immune to anodic dissolution within the physiological potential range [27], shows excellent biocompatibility, and contributes no ionic species of toxicological relevance. A continuous Au interlayer therefore introduces a noble discontinuity at the base of the columnar structure: even if the electrolyte percolates through the intercolumnar boundaries

of the TaN, it encounters at the end of its path not a reactive substrate but a surface that does not dissolve. Gold also acts as a nucleation layer, since a crystalline metallic surface free of native oxide can modify the early growth stages of the nitride and, with them, its phase constitution.

Despite the considerable body of research on Ta and TaN coatings on commercially pure titanium, Ti-6Al-4V and other metallic biomaterials [10,11,27], there is a knowledge gap regarding the behaviour of TaN/Au bilayer systems deposited on the near- β Ti-13Nb-13Zr alloy. In particular, no studies have combined the assessment of long-term electrochemical stability, tribocorrosion mechanisms, metal ion release and biological response for a single system under simulated physiological conditions, in such a way that the complete causal chain from coating architecture to biological outcome can be traced.

Accordingly, the present work evaluates the influence of a gold interlayer on the structural, electrochemical, tribocorrosion and biological behaviour of TaN coatings deposited by magnetron sputtering on aged Ti-13Nb-13Zr alloy. It is hypothesised that the Au interlayer increases the interfacial stability of the coating, reduces surface degradation under tribocorrosion conditions, minimises ion release and, as a consequence, preserves the cytocompatibility of the system. The experimental design was arranged so that the presence of the interlayer was the only variable between the two coated systems, and the results are presented in the sequence of structure, interface, electrochemical behaviour, tribocorrosion, ion release and cellular response, in order to establish the links between scales explicitly.

2. Materials and Methods

2.1. Substrate Preparation

The near- β Ti-13Nb-13Zr alloy was selected as the base material because of its low elastic modulus and high biocompatibility. Specimens were obtained from rolled Ti-13Nb-13Zr bars (nominal composition: 13 wt.% Nb, 13 wt.% Zr, balance Ti) machined into discs 15 mm in diameter and 3 mm thick.

To obtain a stable and homogeneous microstructure before deposition, the samples were heat-treated. The material was solution-treated at 750 °C for 1 h under an argon atmosphere, quenched in distilled water and subsequently aged at 500 °C for 4 h.

Prior to deposition, all samples were metallographically prepared by sequential grinding with silicon carbide papers of 320, 600, 800, 1200, 2000 and 2500 grit, followed by mechanical polishing with 3 μm and 1 μm diamond suspensions and final polishing with 0.05 μm colloidal silica to a mirror finish.

After polishing, the specimens were ultrasonically cleaned for 10 min each in acetone, absolute ethanol and deionised water. They were finally dried with high-purity nitrogen and immediately introduced into the deposition chamber to minimise growth of the native passive titanium oxide layer.

The initial surface roughness was $R_a = 12 \pm 2$ nm over a 45×45 μm^2 scan area, consistent with a polished surface suitable for homogeneous nucleation of the coating.

2.2. Thin-Film Deposition

TaN/Au bilayer coatings were deposited on the polished and cleaned Ti-13Nb-13Zr substrates by magnetron sputtering, using gold (99.99% purity) and tantalum (99.95% purity) targets. The chamber was evacuated to a base pressure of the order of 10^{-6} mbar to reduce the presence of oxygen, water vapour and other residual gases.

Before layer growth, the substrate surfaces underwent in situ ion cleaning by Ar^+ bombardment in order to partially remove the native oxide and activate the surface. The gold interlayer was deposited by non-reactive sputtering, with the deposition time adjusted

to obtain a nominal thickness of 100 nm, chosen to form a continuous interlayer without excessively increasing the metallic fraction of the system. The TaN top layer was then deposited by reactive sputtering in an Ar/N₂ mixture, under conditions selected to promote the formation of tantalum nitride without driving the target into the poisoned regime, and with a negative substrate bias intended to increase the energy of the incident species and promote coating densification while avoiding excessive residual stresses. The full set of process parameters is summarised in Table 1.

Table 1. Magnetron sputtering deposition parameters.

TaN Layer	Au Interlayer	Ar ⁺ Ion Cleaning	Parameter
Ta (99.95%)/Ar + N ₂	Au (99.99%)/Ar	—/Ar	Target/gas
150	100	—	Discharge power (W)
3.0×10^{-2}	5.0×10^{-3}	1.0×10^{-2}	Working pressure (mbar)
9	20	20	Ar flow (sccm)
7	—	—	N ₂ flow (sccm)
43.8	—	—	N ₂ fraction (%)
−75	0	−500	Substrate bias (V)
200	200	—	Substrate temperature (°C)
120	120	—	Target–substrate distance (mm)
10	10	—	Substrate holder rotation (rpm)
Adjusted for 1.80 µm	Adjusted for 100 nm	10 min	Duration
1.80 ± 0.07 µm	100 ± 8 nm	—	Resulting thickness

The process parameters listed in Table 1 were selected on the basis of previous studies on the reactive sputtering of TaN and on noble-metal interlayers, and were refined in preliminary deposition runs. An N₂ fraction of 43.8% was chosen because, for Ta targets, N₂/Ar ratios in this range favour the formation of δ-TaN while avoiding the amorphous or over-stoichiometric films obtained at higher nitrogen contents [28–30]. The discharge power and working pressure were set to keep the Ta target in the transition regime between the metallic and poisoned modes, and the substrate temperature of 200 °C and target–substrate distance of 120 mm were chosen to obtain dense columnar growth at the boundary between zones 1 and T of the structure zone model [31]. A moderate bias of −75 V was applied to densify the film by ion bombardment without generating the high compressive stresses and loss of crystallinity associated with larger bias values [32]. The conditions for the Au interlayer were adapted from previous work on Au-based bilayers for biomedical implants [32–35].

The thickness of each layer was controlled through the deposition time, which was adjusted on the basis of preliminary depositions carried out under the same conditions, and was subsequently verified on cross-sectional SEM micrographs of fractured specimens as described in Section 2.3; the measured values are reported in Table 2. A TaN thickness of about 1.8 µm was targeted as a compromise between load-bearing capacity under sliding contact and the build-up of residual stress, whereas 100 nm was selected for the Au interlayer as a thickness reported to be sufficient to form a continuous, pore-sealing interlayer [26] while keeping the metallic fraction of the system low.

Table 2. Morphological properties of the coatings.

R _q (nm)	R _a (nm)	TaN Thickness (µm)	Au Thickness (nm)	Sample
16 ± 2	12 ± 2	—	—	Ti-13Nb-13Zr
38 ± 5	29 ± 4	1.80 ± 0.07	—	TaN
31 ± 4	23 ± 3	1.80 ± 0.07	100 ± 8	TaN/Au

Before each deposition, the Au and Ta targets were pre-sputtered for 7 min with the shutters closed to remove surface contaminants. After deposition, the samples were cooled inside the chamber to below 50 °C before being exposed to air.

Three experimental groups were prepared: uncoated Ti-13Nb-13Zr substrate, monolithic TaN coating and TaN/Au bilayer system. The monolithic coating was deposited under conditions identical to those of the top layer of the bilayer system, so that the presence of the metallic interlayer was the only variable between the two groups.

2.3. Structural and Morphological Characterisation

The crystal structure was analysed by X-ray diffraction (XRD) on a PANalytical X'Pert PRO diffractometer (Malvern Panalytical, Almelo, The Netherlands) with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) operated at 40 kV and 40 mA. Diffractograms were recorded over the 2θ range of 20–90° with a step size of 0.02° and a counting time of 1 s per step. Phase identification was performed using HighScore Plus software, version 5.3a (Malvern Panalytical, Almelo, The Netherlands), in conjunction with the ICDD PDF-4+ database. The mean crystallite size was estimated with the Scherrer equation from the δ -TaN (111) reflection, using $K = 0.9$.

Surface morphology and cross-sections were examined by scanning electron microscopy (SEM; FEI Quanta 200, Thermo Fisher Scientific, Hillsboro, OR, USA) at accelerating voltages of 15–20 kV. The thickness of the TaN coating was determined from cross-sectional micrographs of fractured specimens by averaging at least ten measurements per sample. The elemental distribution across the coating–substrate interface was examined by energy-dispersive X-ray spectroscopy (EDS) mapping of Ta, Au and Ti on the cross-section of the TaN/Au system (Figure 1). Because the Au interlayer is close to the spatial resolution of SEM-EDS, its thickness is reported as a nominal value estimated from the calibrated deposition rate and deposition time.

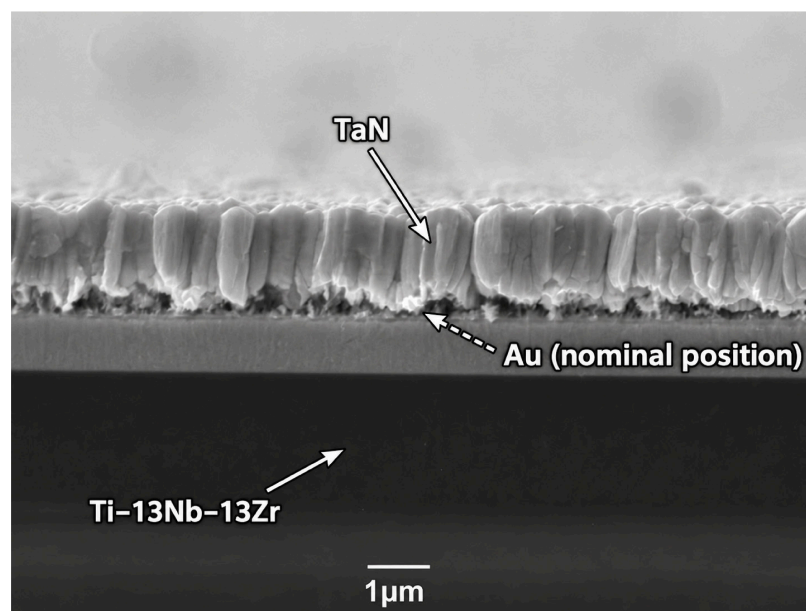


Figure 1. Cross-sectional SEM micrograph of the TaN/Au system deposited on Ti-13Nb-13Zr, showing the columnar TaN top layer, the Au interlayer (indicated by arrows) and the Ti-13Nb-13Zr substrate; the inset shows the corresponding EDS elemental map of Ta, Au and Ti across the interface. Scale bar: 1 μm .

Surface topography was characterised by atomic force microscopy (AFM; Dimension Icon, Bruker, Santa Barbara, CA, USA) in tapping mode over $45 \times 45 \mu\text{m}^2$ areas. The arithmetic mean roughness (R_a) and root-mean-square roughness (R_q) were calculated as

the average of at least five regions per condition, after first-order plane correction to remove sample-holder tilt.

2.4. Electrochemical Characterisation

Electrochemical behaviour was evaluated in Ringer's lactate solution at 37 ± 0.5 °C using a Gamry Reference 600+ potentiostat/galvanostat (Gamry Instruments, Warminster, PA, USA) and a conventional three-electrode cell. The sample (coated or uncoated) served as the working electrode, with an exposed area of 1 cm^2 delimited by epoxy resin encapsulation; an Ag/AgCl (3 M KCl) electrode was used as the reference and a platinum mesh as the counter electrode.

Before each test, the samples were immersed in the solution for 1 h to allow the open-circuit potential (OCP) to stabilise. Potentiodynamic polarisation curves were recorded from -250 to $+250$ mV relative to the OCP at a scan rate of $1 \text{ mV}\cdot\text{s}^{-1}$. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were estimated by extrapolating the approximately linear portions of the cathodic and anodic branches adjacent to E_{corr} . The polarisation resistance (R_p) was subsequently calculated using the Stern–Geary relationship. The selected potential interval was intended to provide a comparative assessment of the electrochemical behaviour of the uncoated and coated systems under conditions close to their free-corrosion potentials, rather than to characterise their complete passive, transpassive or breakdown behaviour. Within this restricted potential interval, no sufficiently defined passive-current plateau or breakdown transition was observed; consequently, i_{pass} and E_b could not be determined reliably and are not reported. The resulting I_{corr} values should therefore be interpreted as comparative electrochemical estimates rather than as absolute corrosion rates.

Electrochemical impedance spectroscopy (EIS) was performed by applying a 10 mV sinusoidal perturbation around the OCP between 100 kHz and 10 mHz. The spectra were fitted using the equivalent circuit, $R_s - [CPE_{\text{coat}} \parallel (R_{\text{coat}} - (CPE_{\text{dl}} \parallel R_{\text{ct}}))]$, which is commonly used for porous PVD coatings on passivating substrates [15,26]. In this circuit, R_s is the solution resistance; CPE_{coat} and R_{coat} describe the capacitive response of the coating and the ionic resistance of the electrolyte within its through-thickness pores and defects, respectively; and CPE_{dl} and R_{ct} describe the double layer and the charge-transfer resistance at the substrate area exposed at the base of these defects. Constant phase elements were used instead of ideal capacitors to account for surface heterogeneity, with impedance $Z_{\text{CPE}} = 1/[Q(j\omega)^{n^*}]$. The polarisation resistance R_p is obtained from the polarisation curves by the Stern–Geary equation and is not an element of this circuit. The goodness of fit was assessed by the χ^2 parameter. For the uncoated substrate, which has no coating layer, a single-time-constant circuit $R_s - (CPE_{\text{dl}} \parallel R_{\text{ct}})$ was used. All measurements were performed in triplicate on independent samples.

2.5. Tribocorrosion Tests

Tribocorrosion tests were performed using a reciprocating tribometer (T50, NANOVEA Inc., Irvine, CA, USA) coupled to a conventional three-electrode electrochemical cell. The tests were conducted following the ASTM G119 guide [29] and the approach proposed by Mischler [12] to separate the contributions of mechanical wear, electrochemical corrosion and the synergistic interaction between the two. A 6 mm diameter Al_2O_3 ball was used as the counterbody. Tests were run under a normal load of 5 N, a frequency of 1 Hz and a stroke length of 5 mm up to a total sliding distance of 1000 m. These conditions correspond to 100,000 cycles, a duration of approximately 27.8 h and a mean sliding speed of $10 \text{ mm}\cdot\text{s}^{-1}$. All experiments were carried out in Ringer's lactate solution at 37 °C.

Three types of test were performed to determine the contribution of each mechanism to the total material loss: (i) sliding under cathodic protection at -0.82 V vs. Ag/AgCl (saturated KCl), a condition selected to minimise electrochemical dissolution and determine the predominantly mechanical wear (W_0); (ii) static immersion, without sliding and for the same duration as the tribological test, to determine the material loss due solely to corrosion (C_0); and (iii) sliding under potentiostatic control in the passive region, with continuous recording of the anodic current during contact to calculate the electrochemical loss by Faraday's law.

The total material loss was decomposed according to

$$T = W_0 + C_0 + S, \quad (1)$$

where T is the total material loss and S is the synergistic term. The latter was calculated as

$$S = \Delta W_c + \Delta C_w, \quad (2)$$

where ΔW_c is the corrosion-induced increase in wear and ΔC_w is the wear-induced increase in corrosion.

The coefficient of friction and the electrochemical response were recorded continuously throughout the tests. After testing, the wear tracks were characterised using a three-dimensional non-contact optical profilometer (PS50, NANOVEA Inc., Irvine, CA, USA). Wear volume was calculated by numerical integration of the surface located below the mean unworn reference plane surrounding the wear track. At least three representative regions distributed along each wear track were analysed. Three independent tests were performed for each experimental condition, and the results are reported as the mean $\pm$ standard deviation.

Following profilometric characterisation, representative regions of the wear tracks were examined using the SEM described in Section 2.3 at a magnification of $\times 500$. The SEM observations were used to identify the predominant wear morphology and to complement the quantitative wear-volume measurements. Because no EDS analysis or compositional mapping of the worn surfaces was performed, the micrographs were not used to determine whether the TaN coating was completely penetrated or whether the nominal Au interlayer or Ti-13Nb-13Zr substrate became locally exposed.

2.6. Metal Ion Release (ICP-MS)

The release of metallic species was evaluated by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7900, Agilent Technologies, Tokyo, Japan). Each sample was immersed individually in 20 mL of sterile Ringer's lactate solution at 37°C for 1, 7, 15 and 30 days. Independent samples were used for each exposure interval and the medium was not renewed during the test; the values obtained therefore represent the cumulative release up to each time point. At the end of each interval, the solution was collected and acidified with ultrapure nitric acid to a final concentration of 2% (v/v).

2.7. Cytotoxicity Assays

The biological response was evaluated using the MG-63 cell line, derived from human osteosarcoma and widely used as an osteoblast-like model in studies of orthopaedic biomaterials. The assays were performed in accordance with ISO 10993-5 [30] by indirect contact with sample extracts. All samples were first sterilised by immersion in 70% ethanol, followed by ultraviolet irradiation for 30 min on each side.

Extracts were prepared at a sample surface area to medium volume ratio of $3\text{ cm}^2\cdot\text{mL}^{-1}$ and held for 24 h at 37°C , in accordance with ISO 10993-12 [31]. Cells were seeded in 24-well culture plates at a density of 1×10^4 cells $\cdot\text{cm}^{-2}$ in DMEM supplemented

with 10% foetal bovine serum and 1% penicillin/streptomycin, at 37 °C, 5% CO₂ and 95% relative humidity.

Cell viability was determined by the MTT assay after 24, 48 and 72 h of incubation, by measuring the absorbance at 570 nm and expressing the results as a percentage of the control. Cell membrane integrity was assessed by lactate dehydrogenase (LDH) release, read at 490 nm. Cells cultured in complete medium without exposure to the sample extracts served as the negative control, and cells treated with 0.1% Triton X-100 to induce cell lysis served as the positive control.

3. Results and Discussion

3.1. Coating Thickness and Morphology

Figure 1 shows the cross-sectional micrograph of the TaN/Au system deposited on the near- β Ti-13Nb-13Zr alloy. The coating provided continuous coverage over the entire surface analysed, with no delamination, through-thickness cracking or spallation, indicating adequate stability during deposition and metallographic preparation.

The cross-section revealed a well-defined columnar microstructure with a mean column width of 850 ± 15 nm, consistent with the transition between zones 1 and T of Thornton's structure zone model, characteristic of growth at low homologous temperature [33]. The thickness of the ceramic layer was 1.80 ± 0.07 μ m, obtained from ten measurements distributed across the cross-section.

A contrast band can be distinguished at the coating–substrate interface (arrows in Figure 1). The cross-sectional EDS map (inset) shows a Au-rich region located between the Ta-rich coating and the Ti-rich substrate, allowing the TaN top layer and the Au interlayer to be differentiated. Given the nominal thickness of the interlayer (100 ± 8 nm), which is close to the spatial resolution of SEM-EDS, the map confirms its position within the coating stack, whereas a detailed assessment of its lateral continuity at the nanometre scale would require TEM analysis.

From a functional standpoint, the columnar nature of the coating is decisive for everything that follows. In PVD systems, intercolumnar boundaries, pores and growth defects allow the electrolyte to reach the metallic substrate. A galvanic couple is then formed between a large cathode, the conductive ceramic coating, and a small anode, the substrate exposed at the base of the defect. This configuration accelerates localised corrosion and tribocorrosion-driven degradation [31]. In this context, the role attributed to the Au interlayer is not limited to improving adhesion; rather, it would interrupt the continuity of these pathways to the substrate: even if the electrolyte reached the base of the TaN columns, it would encounter a noble metallic layer that does not dissolve within the physiological potential range, so that the galvanic couple would not be established on the alloy.

Surface topography is shown in Figure 2. After first-order plane correction, R_a values of 12 ± 2 nm were obtained for the substrate, 29 ± 4 nm for TaN and 23 ± 3 nm for TaN/Au; the corresponding R_q values were 16 ± 2 , 38 ± 5 and 31 ± 4 nm (Table 2).

The polished substrate retains residual grooves from the polishing process, whereas the coated surfaces show a homogeneous granular texture arising from the columnar growth observed in cross-section, with no local material build-up or large-scale defects. The increase in roughness relative to the polished substrate is expected and is associated with the development of crystalline grains during deposition. It is noteworthy, however, that the bilayer system shows a roughness approximately 20% lower than that of the monolithic coating deposited under identical conditions: the only difference between the two is the surface on which the TaN nucleates.

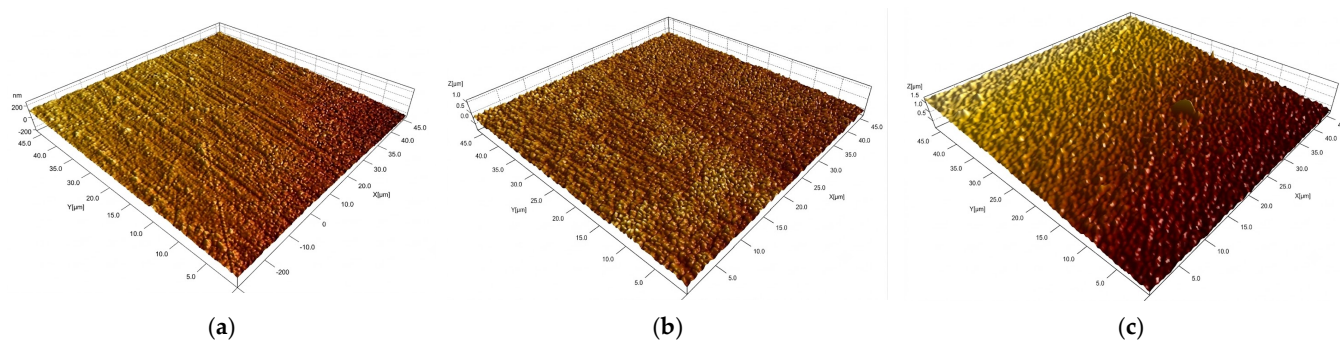


Figure 2. AFM topographic images over $45 \times 45 \mu\text{m}^2$ areas: (a) Ti-13Nb-13Zr; (b) TaN; (c) TaN/Au.

3.2. Crystalline Phase Analysis (XRD)

The diffractograms of the three conditions are shown in Figure 3, and the derived structural parameters are summarised in Table 3. For the substrate, the β -Ti (110), (200) and (211) reflections were identified as predominant.

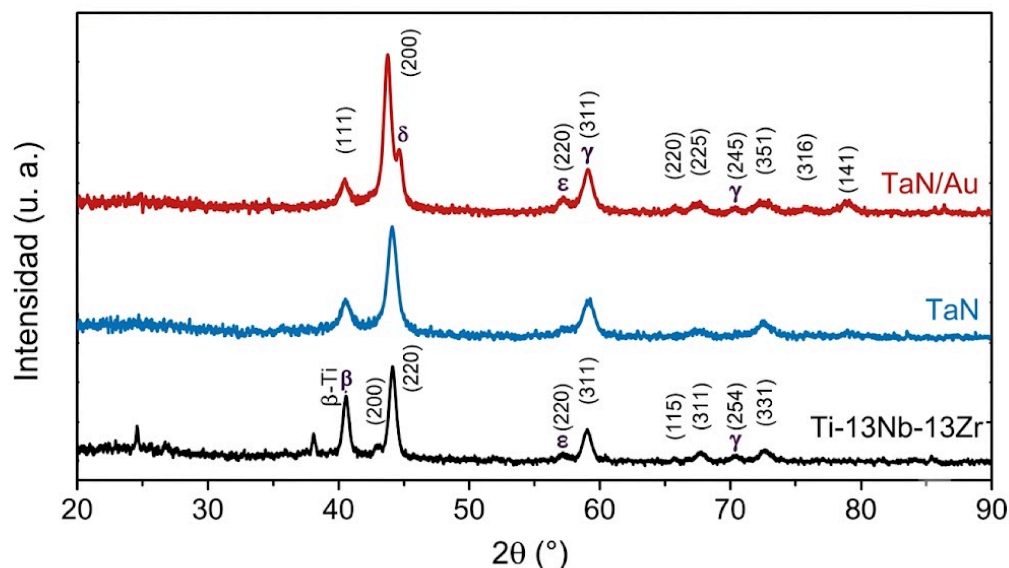


Figure 3. X-ray diffractograms of the Ti-13Nb-13Zr substrate, the monolithic TaN coating and the TaN/Au bilayer system.

Table 3. Structural parameters obtained by XRD.

Preferred Orientation	FWHM (°)	Crystallite Size (nm)	Identified Phases	Sample
–110	—	—	β -Ti	Ti-13Nb-13Zr
–111	0.39	24 ± 3	δ -TaN + ϵ -TaN + γ -Ta ₂ N	TaN
–111	0.31	31 ± 2	δ -TaN + Au (ϵ -TaN and γ -Ta ₂ N attenuated)	TaN/Au

After deposition, the pattern changed substantially owing to the appearance of reflections from the Ta–N system. In the monolithic TaN coating, the (111), (200), (220) and (311) peaks of the cubic δ -TaN phase were identified as the major component, accompanied by lower-intensity signals corresponding to ϵ -TaN and γ -Ta₂N. This coexistence of phases is consistent with the N₂/Ar ratio used during reactive sputtering: the available nitrogen initially favours the formation of Ta₂N, whereas a progressive increase in nitrogen concentration successively stabilises the ϵ -TaN and δ -TaN phases [19,23].

In the TaN/Au sample, the ϵ -TaN and γ -Ta₂N reflections were markedly attenuated, indicating a higher relative fraction of δ -TaN. The crystallite size estimated with the Scherrer

equation from δ -TaN (111) increased from 24 ± 3 nm for TaN to 31 ± 2 nm for TaN/Au, with a decrease in FWHM from 0.39° to 0.31° . Since both coatings were deposited under identical process conditions, this difference can be attributed mainly to the nature of the nucleation surface: metallic Au, crystalline and free of native oxide, provides an energetically more homogeneous growth template than the alloy surface, which retains a residual oxide despite ion cleaning. This reduces the density of competing nucleation sites and allows the development of larger crystallites and a more uniform phase constitution.

The predominance of δ -TaN is particularly favourable for biomedical applications, as this phase combines high hardness, good chemical stability and resistance to corrosion and wear [31]. Nevertheless, the most relevant argument for this work is electrochemical: reducing the minority phases eliminates interfaces between domains of differing nobility which, in multiphase systems, act as preferential sites for localised attack and as galvanic microcells within the coating itself. The Au interlayer therefore not only blocks the path of the electrolyte to the substrate but also reduces the number of susceptible sites within the ceramic layer.

3.3. Electrochemical Behaviour

The potentiodynamic polarisation curves of the three conditions are shown in Figure 4, and the parameters obtained by Tafel extrapolation are summarised in Table 4.

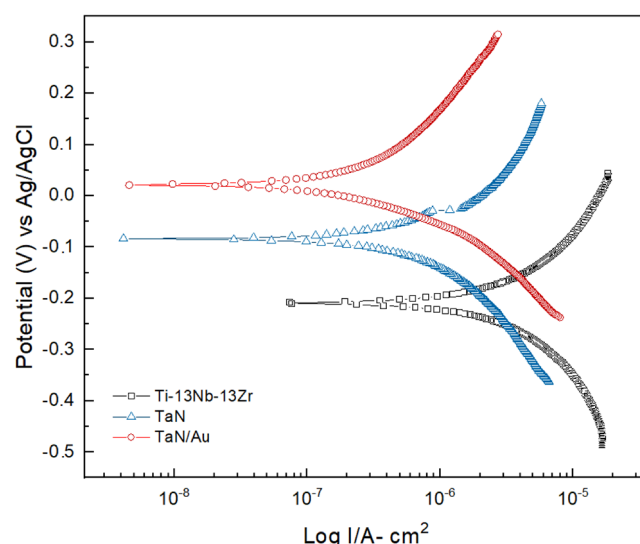


Figure 4. Potentiodynamic polarisation curves of the three conditions in Ringer's lactate at 37°C .

The bare substrate exhibited $E_{\text{corr}} = -210 \pm 18$ mV (all potentials are referred to Ag/AgCl), $I_{\text{corr}} = 0.42 \pm 0.06 \mu\text{A}\cdot\text{cm}^{-2}$ and $R_p = 62 \pm 9 \text{ k}\Omega\cdot\text{cm}^2$, values typical of a passivating alloy whose protection relies on an oxide film only a few nanometres thick. The monolithic coating shifted the corrosion potential to -85 ± 12 mV and lowered the current density to $0.075 \pm 0.010 \mu\text{A}\cdot\text{cm}^{-2}$, a 5.6-fold decrease, with $R_p = 340 \pm 35 \text{ k}\Omega\cdot\text{cm}^2$. The bilayer system gave the most favourable response on all three metrics simultaneously: $E_{\text{corr}} = +35 \pm 10$ mV, $I_{\text{corr}} = 0.018 \pm 0.004 \mu\text{A}\cdot\text{cm}^{-2}$ and $R_p = 1420 \pm 150 \text{ k}\Omega\cdot\text{cm}^2$, representing a 23-fold reduction in current density relative to the substrate and a 4.2-fold reduction relative to monolithic TaN [36].

To compare the corrosion resistance of the coatings quantitatively, the protection efficiency (PE) was calculated from the corrosion current densities as $PE (\%) = [(I_{\text{corr},s} - I_{\text{corr},c}) / I_{\text{corr},s}] \times 100$, where $I_{\text{corr},s}$ and $I_{\text{corr},c}$ are the corrosion current densities of the uncoated substrate and of the coated sample, respectively. PE values of 82.1% and 95.7% were obtained for TaN and TaN/Au, respectively. In addition, the corrosion

rate (CR) was estimated according to ASTM G102 [37] as $CR = K_1 \cdot (I_{\text{corr}}/\rho) \cdot EW$, with $K_1 = 3.27 \times 10^{-3} \text{ mm} \cdot \text{g} \cdot \mu\text{A}^{-1} \cdot \text{cm}^{-1} \cdot \text{year}^{-1}$, an equivalent weight $EW = 13.4 \text{ g} \cdot \text{equiv}^{-1}$ (assuming oxidation to Ti^{4+} , Nb^{5+} and Zr^{4+}) and a density $\rho = 5.0 \text{ g} \cdot \text{cm}^{-3}$ for Ti-13Nb-13Zr. Since dissolution in the coated samples is assumed to take place on the alloy exposed at the base of coating defects, the same EW and ρ were used for the three conditions, giving $CR \approx 3.7 \times 10^{-3}$, 6.6×10^{-4} and $1.6 \times 10^{-4} \text{ mm} \cdot \text{year}^{-1}$ for Ti-13Nb-13Zr, TaN and TaN/Au, respectively. Consistent with the caveat stated in Section 2.4, these values are comparative indicators rather than absolute penetration rates. The polarisation resistance increased by factors of 5.5 and 22.9 relative to the substrate, in close agreement with the reductions in I_{corr} (5.6- and 23-fold), which confirms the internal consistency of the Tafel and Stern–Geary analyses.

The anodic shift in the corrosion potential is as informative as the reduction in current. A ceramic coating that merely covered the surface without modifying the nature of the interface would retain an E_{corr} close to that of the substrate, since the anodic reaction would still take place on the alloy exposed at the defects. The +245 mV shift observed for TaN/Au indicates that the species governing the equilibrium at the interface has changed, and is consistent with the presence of a noble interlayer accessible to the electrolyte through the residual porosity of the TaN [32].

Electrochemical impedance spectroscopy confirmed this trend. The Nyquist plots (Figure 5) showed capacitive arcs with increasing diameters in the order Ti-13Nb-13Zr < TaN < TaN/Au, indicating a progressive reduction in interfacial electrochemical activity [33]. The spectra were satisfactorily fitted using the equivalent circuit shown in Figure 6, with χ^2 values below 1×10^{-3} in all cases. The fitted EIS parameters, including the Q and n values associated with the coating and double-layer constant phase elements, are reported in Table 4b. The charge-transfer resistance increased from $12 \pm 1 \text{ k}\Omega \cdot \text{cm}^2$ for the uncoated substrate to $62 \pm 5 \text{ k}\Omega \cdot \text{cm}^2$ for TaN and $129 \pm 10 \text{ k}\Omega \cdot \text{cm}^2$ for TaN/Au. The uncertainties correspond to the standard deviations obtained from three independently fitted spectra rather than to the formal errors generated by the fitting software. For the uncoated substrate, no coating-related time constant is present, and the spectra were therefore fitted with the simplified $R_s\text{--}(\text{CPE}_{\text{dl}}\parallel R_{\text{ct}})$ circuit. The decrease in Q_{coat} from 3.2×10^{-6} to $1.4 \times 10^{-6} \text{ S} \cdot \text{s}^n \cdot \text{cm}^{-2}$, together with the increase in n_{coat} from 0.84 to 0.90, indicates a smaller electrolyte-accessible area and a more homogeneous coating for the bilayer system, in agreement with its higher R_{coat} .

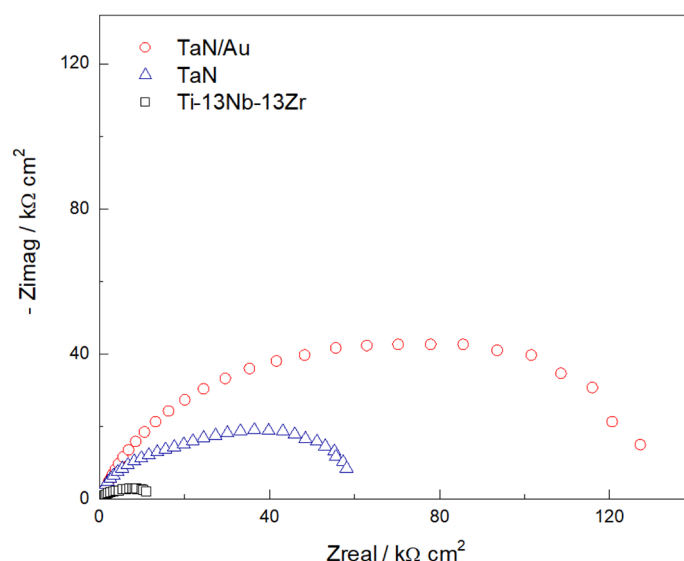


Figure 5. Nyquist diagrams of the three conditions in Ringer’s lactate at 37 °C.

The fitted parameters provide further insight into the protective behaviour of the coatings. R_{coat} , associated with electrolyte penetration through pores and other conductive defects in the coating, increased by a factor of approximately 2.6, from $420 \Omega \cdot \text{cm}^2$ for TaN to $1100 \Omega \cdot \text{cm}^2$ for TaN/Au. This increase indicates greater opposition to electrolyte transport through the bilayer and is consistent with a reduction in the number, connectivity or effective conductivity of through-thickness defects. Likewise, R_{ct} increased by a factor of approximately 2.1, from 62 to $129 \text{ k}\Omega \cdot \text{cm}^2$, demonstrating that the TaN/Au architecture also hindered the interfacial charge-transfer reaction. The two resistance components therefore describe complementary contributions to the protective response: electrolyte transport through coating defects and the electrochemical reaction occurring at the underlying interface. Although the presence of Au may contribute to the lower interfacial reactivity, the EIS results alone do not demonstrate that the nominal Au layer forms a completely continuous barrier.

The R_{coat} values are considerably lower than the corresponding R_{ct} values, which is consistent with the physical interpretation of this element in the nested equivalent circuit. R_{coat} does not represent the intrinsic bulk resistance of the TaN ceramic layer. Instead, it represents the effective resistance associated with electrolyte penetration through pores and other permeable defects in the coating. The contribution of such defects to the impedance response of PVD ceramic coatings has previously been described using equivalent-circuit models [26]. In the present systems, R_{ct} was approximately two orders of magnitude greater than R_{coat} , indicating that the low-frequency interfacial charge transfer process provided the dominant resistive contribution to the measured electrochemical response.

To assess whether the additional coating-related time constant was justified, the spectra were also fitted using the simplified R_s -(CPE||R) circuit, in which the high-frequency coating contribution was omitted. For TaN and TaN/Au, the simplified model yielded χ^2 of 2.4×10^{-3} and 3.1×10^{-3} , respectively, compared with 4.8×10^{-4} and 3.9×10^{-4} for the nested circuit. The lower χ^2 values obtained with the nested circuit, together with its improved reproduction of the high-frequency feature in the Bode phase plots, support the inclusion of the coating-related R_{coat} -CPE time constant. In addition, the simplified circuit did not adequately reproduce the high-frequency feature observed in the Bode phase plots. These results support the inclusion of the R_{coat} -CPE time constant in the equivalent circuit used in Figure 6. The fitted Q and n parameters for both time constants are included in Table 4b.

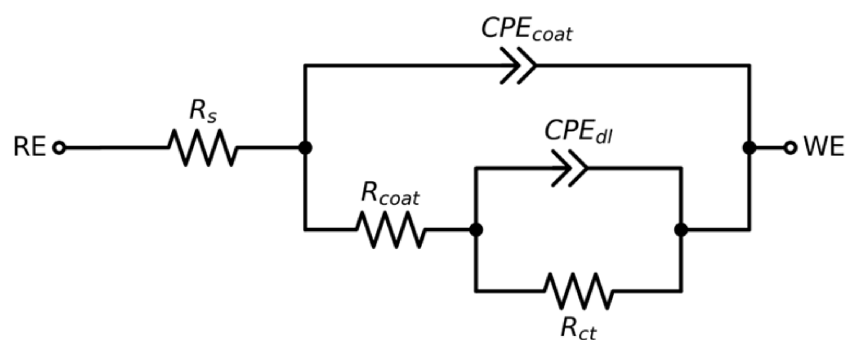


Figure 6. Equivalent circuit R_s -[CPE_{coat} ||(R_{coat} -(CPE_{dl} || R_{ct}))] used to fit the electrochemical impedance spectra: R_s , solution resistance; CPE_{coat} and R_{coat} , coating capacitance and pore resistance; CPE_{dl} and R_{ct} , double-layer capacitance and charge-transfer resistance.

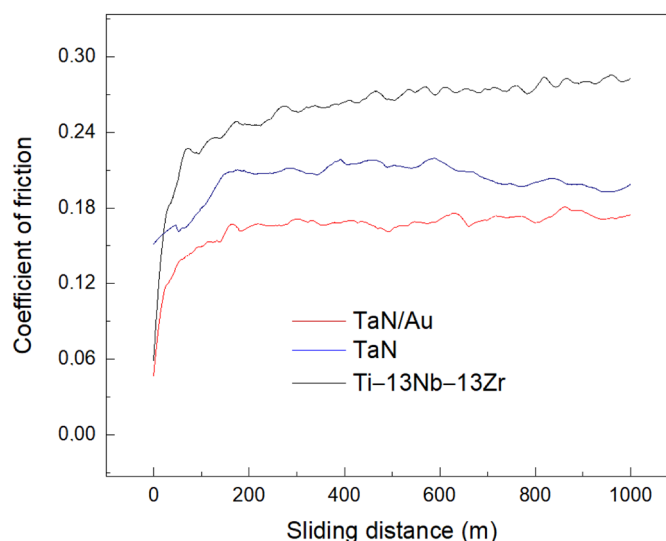
Table 4. Electrochemical parameters of the three conditions in Ringer's lactate at 37 °C: (a) potentiodynamic polarisation; (b) EIS fitting with the circuit in Figure 6.

(a)						
Sample	E_{corr} (mV vs. Ag/AgCl)	I_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	R_{p} ($\text{k}\Omega\cdot\text{cm}^2$)	PE (%)		
Ti-13Nb-13Zr	-210 ± 18	0.42 ± 0.06	62 ± 9	—		
TaN	-85 ± 12	0.075 ± 0.010	340 ± 35	82.1		
TaN/Au	$+35 \pm 10$	0.018 ± 0.004	1420 ± 150	95.7		
(b)						
Sample	Q_{coat} ($\text{S}\cdot\text{s}^n\cdot\text{cm}^{-2}$)	n_{coat}	R_{coat} ($\Omega\cdot\text{cm}^2$)	Q_{dl} ($\text{S}\cdot\text{s}^n\cdot\text{cm}^{-2}$)	n_{dl}	R_{ct} ($\text{k}\Omega\cdot\text{cm}^2$)
Ti-13Nb-13Zr	—	—	—	$(8.0 \pm 1.1) \times 10^{-5}$	0.79 ± 0.03	12 ± 1
TaN	$(3.2 \pm 0.5) \times 10^{-6}$	0.84 ± 0.02	420 ± 45	$(3.5 \pm 0.6) \times 10^{-5}$	0.84 ± 0.02	62 ± 5
TaN/Au	$(1.4 \pm 0.2) \times 10^{-6}$	0.90 ± 0.02	1100 ± 120	$(1.6 \pm 0.3) \times 10^{-5}$	0.89 ± 0.02	129 ± 10

E_{corr} , I_{corr} and R_p were obtained from the potentiodynamic polarisation curves (Tafel extrapolation and Stern–Geary equation); PE, protection efficiency. The EIS parameters are mean $\pm$ standard deviation of three independently fitted spectra. The uncoated substrate was fitted with a single time constant, R_s –($\text{CPE}_{\text{dl}} \parallel R_{\text{ct}}$).

3.4. Tribocorrosion Behaviour

Figure 7 shows the evolution of the coefficient of friction (COF) during sliding in Ringer's lactate solution. All three conditions exhibited an initial running-in stage, particularly evident during the first 150–200 m, followed by a more gradual evolution. However, the curves do not show a strictly steady-state regime over the entire subsequent interval: the substrate exhibited a progressive increase in friction, whereas the monolithic TaN coating showed a moderate decrease towards the end of the test.

**Figure 7.** Evolution of the coefficient of friction with sliding distance for the three conditions in Ringer's lactate at 37 °C.

Read from the curves, the characteristic COF values were approximately 0.28 for Ti-13Nb-13Zr, 0.20 for TaN and 0.17 for TaN/Au. These values describe the graphical trend and should be distinguished from mean values calculated over a defined analysis interval. The bilayer system exhibited the lowest friction over most of the sliding distance [32–35,38]. The fluctuations observed may be related to changes in contact conditions and surface state; their association with depassivation processes would need to be checked against the simultaneously recorded electrochemical response.

The total volumes of material removed were $(8.6 \pm 0.8) \times 10^{-3} \text{ mm}^3$ for the substrate, $(3.1 \pm 0.4) \times 10^{-3} \text{ mm}^3$ for TaN and $(1.2 \pm 0.2) \times 10^{-3} \text{ mm}^3$ for TaN/Au. On the basis of the central values, the bilayer system showed a removed volume approximately 86% lower than that of the substrate, equivalent to a 7.2-fold reduction.

The interaction between wear and corrosion was analysed with the balance given in Equation (1), where W_0 and C_0 represent the reference contributions of mechanical wear and corrosion, respectively, and S is the interaction term. The values listed in Table 5 place the relative contribution S/T at approximately 35%, 24% and 14% for Ti-13Nb-13Zr, TaN and TaN/Au, respectively. This trend suggests a smaller relative contribution of the interaction between the two processes in the bilayer system, subject to verification of the balance and of the uncertainties of its components.

Table 5. Approximate coefficients of friction and contributions to material loss during tribocorrosion tests in Ringer's lactate at 37 °C.

S/T (%)	Synergy S ($\times 10^{-3} \text{ mm}^3$)	$W_0 + C_0$ ($\times 10^{-3} \text{ mm}^3$)	Total Volume T ($\times 10^{-3} \text{ mm}^3$)	Approx. COF	Sample
35	3	5.6	8.6 ± 0.8	≈ 0.28	Ti-13Nb-13Zr
24	0.74	2.4	3.1 ± 0.4	≈ 0.20	TaN
14	0.17	1	1.2 ± 0.2	≈ 0.17	TaN/Au

The observed behaviour is consistent with greater protection of the TaN/Au system against material loss under the conditions studied. One possible explanation is that the interlayer helps to limit electrolyte access to the substrate through defects in the TaN, provided that it retains its continuity during contact. Nevertheless, the available results do not allow this mechanism to be established unequivocally, nor the reduction in synergy to be attributed exclusively to the presence of Au.

The interpretation must also consider the depth of the wear track relative to the coating thickness. Exposure of the interlayer or the substrate would change the materials present in the contact and, therefore, the degradation processes. Combining three-dimensional profilometry, SEM analysis of the wear tracks and electrochemical records during sliding would allow these possibilities to be assessed.

The SEM micrographs of the wear tracks are presented in Figure 8. The uncoated Ti-13Nb-13Zr alloy exhibited irregular grooves, extensive surface smearing and flake-like regions associated with plastic deformation and local material detachment, indicating a mixed abrasive–adhesive wear mechanism. The TaN-coated surface showed numerous, relatively well-defined grooves aligned with the sliding direction, together with localised debris accumulation, suggesting that abrasive grooving was the predominant material-removal mechanism. In contrast, the TaN/Au system retained a comparatively uniform surface, with fewer longitudinal grooves and only isolated debris particles. No extensive delamination was evident within the particular field examined for the bilayer coating. This progressive reduction in surface damage is consistent with the measured wear volumes and the lower friction displayed by the coated systems.

The interaction between wear and corrosion was analysed using the balance given in Equation (1), where (W_0) and (C_0) represent the reference contributions of mechanical wear and corrosion, respectively, and (S) is the interaction term. The values reported in Table 5 place the relative contribution (S/T) at approximately 35%, 24% and 14% for Ti-13Nb-13Zr, TaN and TaN/Au, respectively. This trend indicates that the relative contribution of wear–corrosion interaction decreased progressively with the application of TaN and the TaN/Au architecture. Nevertheless, this interpretation remains depen-

dent on the validity of the material-loss balance and the uncertainties associated with its individual components.

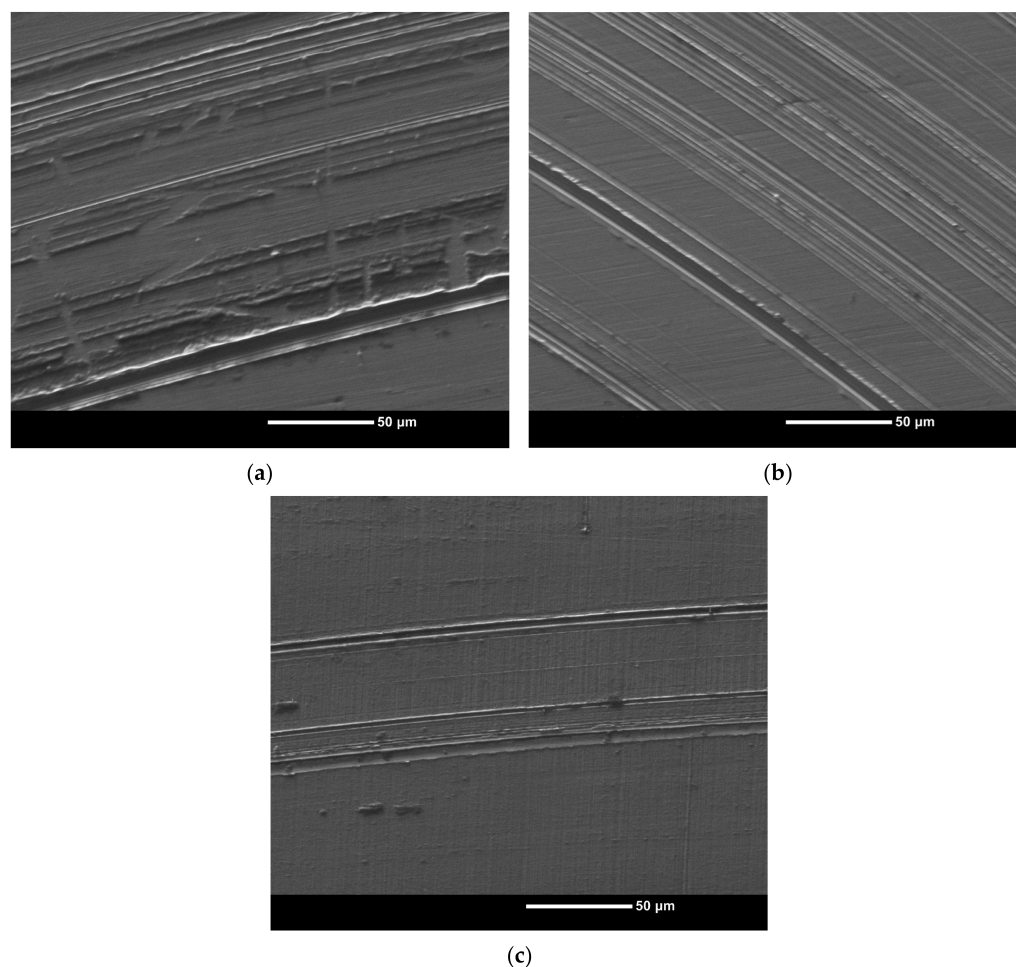


Figure 8. SEM micrographs of the wear tracks formed on: (a) Ti-13Nb-13Zr, (b) TaN and (c) TaN/Au after tribocorrosion testing. The uncoated alloy exhibits pronounced surface smearing, irregular grooves and local material detachment; the TaN coating shows predominantly parallel abrasive grooves and localised debris; and the TaN/Au system retains a comparatively uniform surface with fewer grooves and limited debris accumulation.

The combined friction, wear-volume and SEM results demonstrate that the TaN/Au system provided the greatest resistance to material loss under the investigated conditions. The nominal Au interlayer may contribute to reducing interfacial electrochemical activity when defects develop in the TaN layer. However, the available SEM images do not provide compositional or quantitative depth information and therefore cannot establish whether the TaN coating was fully penetrated or whether the nominal Au interlayer or Ti-13Nb-13Zr substrate became locally exposed. Consequently, the lower synergistic contribution cannot be attributed exclusively to the presence or continuity of Au.

3.5. Metal Ion Release

The cumulative release of metallic species after 30 days of immersion in Ringer's lactate at 37 °C is shown in Figure 9 and Table 6. The bare alloy released $1.85 \mu\text{g}\cdot\text{cm}^{-2}$ of titanium, whereas the monolithic coating reduced this value to $0.42 \mu\text{g}\cdot\text{cm}^{-2}$ and the bilayer system to $0.16 \mu\text{g}\cdot\text{cm}^{-2}$, representing 4.4- and 11.6-fold reductions, respectively. Tantalum release followed the same trend, decreasing from $0.12 \mu\text{g}\cdot\text{cm}^{-2}$ for the monolithic coating to $0.060 \mu\text{g}\cdot\text{cm}^{-2}$ for the bilayer system. Gold from the interlayer was detected at

$0.015 \mu\text{g}\cdot\text{cm}^{-2}$, two orders of magnitude below the titanium released by the bare alloy and at the lower limit of the quantifiable range.

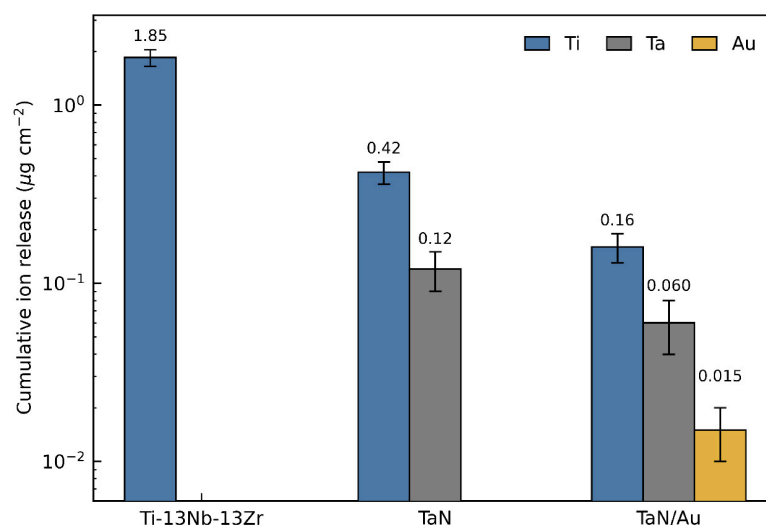


Figure 9. Cumulative metal ion release determined by ICP-MS after 30 days of immersion in Ringer's lactate at 37 °C. Logarithmic scale.

Table 6. Cumulative metal ion release after 30 days of immersion ($\mu\text{g}\cdot\text{cm}^{-2}$).

Reduction Factor vs. Substrate	Total	Au	Ta	Ti	Sample
—	1.85	—	—	1.85 ± 0.20	Ti-13Nb-13Zr
3.4	0.54	—	0.12 ± 0.03	0.42 ± 0.06	TaN
7.9	0.235	0.015 ± 0.005	0.060 ± 0.020	0.16 ± 0.03	TaN/Au

After 30 days of static immersion, the sum of the Ti, Ta and Au masses measured for the bilayer system was $0.235 \mu\text{g}\cdot\text{cm}^{-2}$, compared with $1.85 \mu\text{g}\cdot\text{cm}^{-2}$ of Ti for the uncoated substrate. Considering these elements only, the difference corresponds to a reduction of approximately 87.3%, i.e., a factor of 7.9. This comparison does not necessarily represent the total metal release, since it would require the Nb and Zr results to be incorporated or their exclusion to be justified.

The factor obtained is close to the value of 7.2 calculated for the reduction in volume removed during the tribocorrosion tests. However, the two results stem from independent experimental conditions: metal release was evaluated under static immersion, whereas volume loss was determined under sliding. Their numerical similarity therefore neither demonstrates a causal relationship nor establishes a common degradation mechanism. The results show lower release of the measured elements under static conditions and lower material loss during tribocorrosion for the bilayer system.

The detection of titanium from the coated samples confirms that protection is not absolute and that species are transported through the residual porosity of the coating, as anticipated by the morphological analysis. Nevertheless, the magnitude of the reduction indicates that the bilayer system effectively limits this transport. The most relevant aspect from a toxicological perspective is that the additional species introduced by the new architecture, gold, is released in minimal quantities and is an element with no documented adverse effects at these concentrations, so that the reduction in ionic load is not achieved at the cost of introducing a new risk.

3.6. Cellular Response

The results for cell viability and membrane integrity in MG-63 cells are shown in Figure 10 and Table 7. MTT viability at 72 h was $82 \pm 5\%$ for the bare alloy, $91 \pm 4\%$ for the monolithic coating and $96 \pm 3\%$ for the bilayer system. LDH release followed the inverse trend, decreasing from $18 \pm 3\%$ to $11 \pm 2\%$ and $7 \pm 2\%$, respectively.

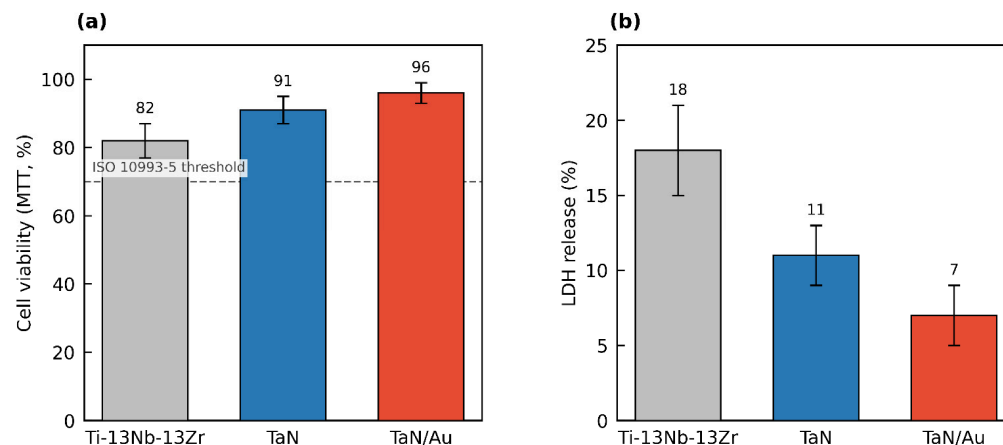


Figure 10. Response of MG-63 cells after 72 h of incubation: (a) viability determined by MTT assay, with the 70% threshold established by ISO 10993-5 indicated; (b) lactate dehydrogenase release.

Table 7. Response of MG-63 cells after 72 h of incubation.

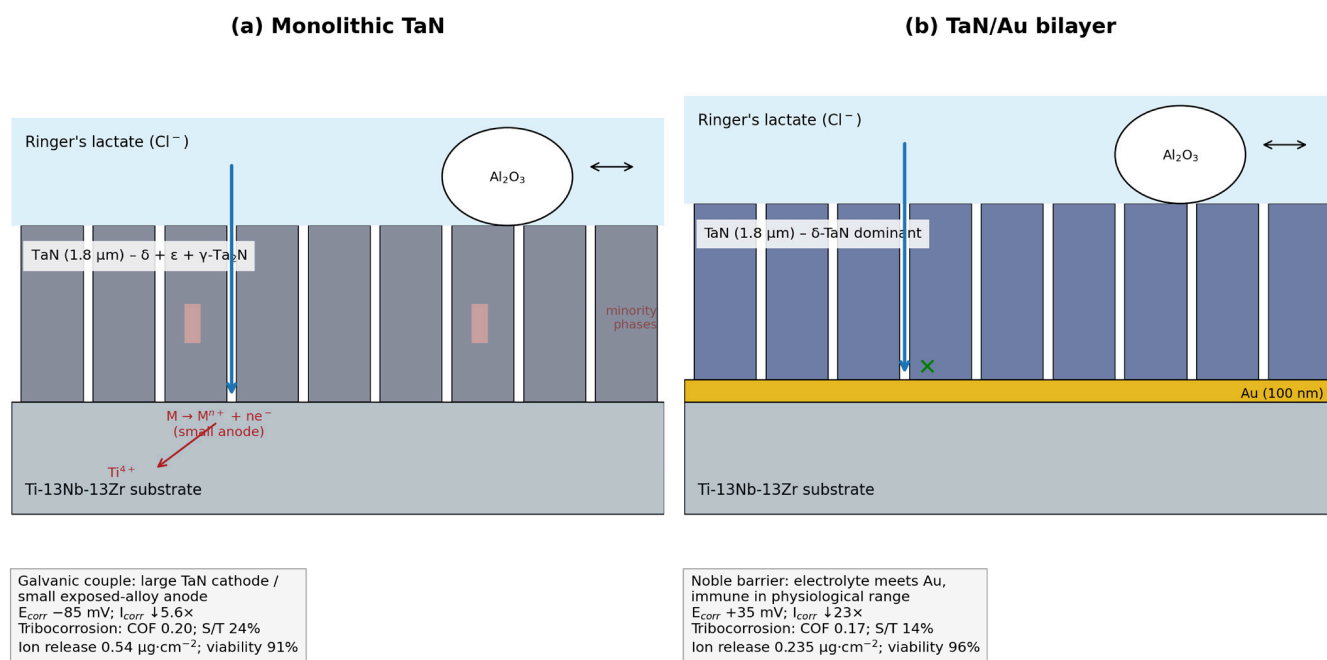
Total Ion Release ($\mu\text{g}\cdot\text{cm}^{-2}$)	LDH Release (%)	MTT Viability (%)	Sample
1.85	18 ± 3	82 ± 5	Ti-13Nb-13Zr
0.54	11 ± 2	91 ± 4	TaN
0.235	7 ± 2	96 ± 3	TaN/Au

All three conditions exceeded the 70% viability threshold established by ISO 10993-5 [30], so none can be classified as cytotoxic. The relevant finding is therefore not compliance with the standard criterion, but the existence of a consistent gradation among the three conditions that mirrors the order observed for ion release: as the total metal load released decreases from 1.85 to 0.54 and $0.235 \mu\text{g}\cdot\text{cm}^{-2}$, viability rises from 82% to 91% and 96%, and LDH release falls from 18% to 11% and 7%. The agreement between an assay of metabolic activity (MTT) and one of membrane integrity (LDH), which probe different cellular mechanisms, strengthens this observation. However, since the extracts were obtained after 24 h of extraction whereas ion release was quantified at 30 days, the correspondence between the two data sets should be regarded as qualitative rather than as an established dose–response relationship.

This result completes the sequence of effects that underpins the work: a modification of the coating architecture at the 100 nm scale is associated with a more homogeneous phase constitution of the ceramic, greater electrochemical stability, weaker coupling between wear and corrosion, a lower ionic load released into the medium and, ultimately, a measurable improvement in the response of osteoblast-like cells. The consistency of this trend across the different scales of analysis constitutes the main contribution of this study.

3.7. Proposed Mechanism

The results presented allow a unified mechanism to be proposed in which the gold interlayer operates simultaneously through three complementary pathways, summarised schematically in Figure 11. Each pathway is linked below to the experimental results that support it.



Pathways: (1) structural – Au template refines TaN growth; (2) noble barrier – blocks galvanic attack; (3) tribo-electrochemical – suppresses depassivation–repassivation

Figure 11. Schematic representation of the proposed mechanism: (a) monolithic TaN, in which the electrolyte percolating through intercolumnar boundaries reaches the alloy and establishes a galvanic couple (large TaN cathode/small alloy anode), with minority Ta–N phases acting as additional local attack sites; (b) TaN/Au bilayer, in which the Au interlayer refines the growth of δ -TaN (structural pathway), stops the electrolyte on a noble surface (noble barrier pathway) and limits depassivation of the substrate during sliding against the Al₂O₃ counterbody (tribo-electrochemical pathway). The key experimental values supporting each pathway are indicated.

Structural pathway. The metallic Au surface, crystalline and free of native oxide, modifies the early nucleation stages of the nitride. The result is a coating with larger crystallites (31 vs. 24 nm), a smaller FWHM, lower surface roughness (R_a of 23 vs. 29 nm) (Figure 2, Table 2) and a phase constitution dominated by δ -TaN, with attenuated ϵ -TaN and γ -Ta₂N (Figure 3, Table 3). As the number of interfaces between domains of differing nobility decreases, so do the internal sites susceptible to localised attack.

Noble barrier pathway. The columnar growth of TaN generates intercolumnar boundaries that act as percolation paths for the electrolyte. It is proposed that the interlayer interrupts the continuity of these paths to the substrate, so that the percolating electrolyte encounters not a passivating alloy susceptible to anodic dissolution but a surface that is immune within the physiological potential range. The presence and position of the interlayer within the coating stack are supported by the cross-sectional EDS map (Figure 1), although its lateral continuity at the nanometre scale has not been verified by TEM (Section 3.1). This pathway is the explanation most consistent with three independent results: the +245 mV shift in E_{corr} (Figure 4, Table 4), the 23-fold reduction in I_{corr} , and the fall in the synergistic fraction under tribocorrosion (Table 5). This interpretation is further supported by the EIS fitting (Figure 5, Table 4), which shows a 2.6-fold higher R_{coat} and an approximately two-fold higher R_{ct} for the bilayer, i.e., a less permeable coating and a less reactive interface at the base of its defects.

Tribo-electrochemical pathway. Under sliding, the absence of an accessible reactive substrate suppresses the depassivation–repassivation cycle that is the dominant source of the synergistic term. The fall in the synergistic fraction from 35% to 14% quantifies this decoupling (Table 5), which is reinforced by the lower coefficient of friction of

the bilayer system (Figure 7), as this reduces the energy dissipated and the severity of mechanical depassivation.

The three pathways converge in the 7.9-fold reduction in the ionic load released into the medium (Figure 9, Table 6), consistent with the improved response of the MG-63 cells (Figure 10, Table 7). The similarity between the reduction in wear volume ($7.2\times$) and that in total ion release under static immersion ($7.9\times$) suggests that both phenomena share a common architectural origin; quantifying the ions released during the tribocorrosion tests themselves would establish what fraction of the ionic load arises from mechanically assisted degradation, an aspect of particular interest for articulating surfaces. From a design perspective, the results indicate that optimising corrosion resistance under static conditions is insufficient unless the tribo-electrochemical coupling is suppressed at the same time.

3.8. Limitations of the Study

The results should be interpreted in light of several limitations. First, the lateral continuity of the Au interlayer was not verified directly; if the interlayer were discontinuous, the regions of exposed alloy in contact with gold could act as anodes of an Au/alloy galvanic couple, a scenario opposite to that proposed, so its characterisation by TEM is a priority. Second, ion release was quantified under static immersion rather than during the tribocorrosion tests, and therefore cannot discriminate the contribution of mechanically assisted degradation. Third, the biological response was evaluated with extracts and with an osteosarcoma-derived cell line whose behaviour does not fully reproduce that of primary osteoblasts; direct-contact assays, osteogenic differentiation assays and studies with primary cells would allow the conclusions to be extended. In addition, the practical adhesion of the coatings was not quantified; scratch testing according to ASTM C1624 [39] would be required to confirm the adhesion-promoting role usually attributed to metallic interlayers. Finally, the tests were carried out with three replicates per condition and in a protein-free medium, whereas the presence of proteins can modify both the corrosion kinetics and the lubrication of the contact [1].

4. Conclusions

This work evaluated the effect of a 100 nm gold interlayer on the surface performance of TaN coatings deposited by magnetron sputtering on aged near- β Ti-13Nb-13Zr alloy. To the authors' knowledge, this is the first study of TaN/Au bilayers on near- β Ti-13Nb-13Zr in which a single system has been followed from coating architecture to electrochemical stability, tribocorrosion, ion release and cellular response. The main conclusions are as follows:

Structural effect. Deposited under identical conditions, a 100 nm Au interlayer acts as a noble, oxide-free growth template for TaN: δ -TaN becomes the dominant phase, the minority ϵ -TaN and γ -Ta₂N phases are attenuated, the crystallite size increases from 24 ± 3 to 31 ± 2 nm and R_a decreases from 29 ± 4 to 23 ± 3 nm.

Corrosion protection. The bilayer shifts E_{corr} from -210 ± 18 to $+35 \pm 10$ mV vs. Ag/AgCl and reduces I_{corr} 23-fold relative to the substrate and 4.2-fold relative to monolithic TaN (protection efficiency of 95.7% vs. 82.1%), with higher R_{coat} and R_{ct} , indicating a less permeable coating and a less reactive interface at the base of its defects.

Tribocorrosion and ion release. Beyond static protection, the bilayer decouples wear and corrosion: the friction coefficient falls from 0.28 to 0.17, the wear volume falls 7.2-fold, and the synergistic fraction falls from 35% to 14%, while the total metal load released falls 7.9-fold and Au release remains at $0.015 \mu\text{g}\cdot\text{cm}^{-2}$.

Biological response and design implications. MG-63 viability increases from $82 \pm 5\%$ to $96 \pm 3\%$ and LDH release decreases from $18 \pm 3\%$ to $7 \pm 2\%$, following the order of ion

release. The novelty of this work lies in showing that a nanometric noble interlayer acts simultaneously on coating growth, on the interfacial electrochemistry, and on the tribo-electrochemical coupling, making it a promising design strategy for articulating surfaces of low-modulus β -titanium alloys.

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