

Article

Ag/ZrO₂ Hybrid Coating for Tribological and Corrosion Protection of Ti45Nb Alloy in Biomedical Environments

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Abstract

In this study, a Ag/ZrO₂ hybrid coating prepared by the sol–gel method on a β -type Ti45Nb alloy was applied by the spin coating technique, and the microstructural, mechanical, electrochemical, and tribological properties of the surface were evaluated in a multi-dimensional manner. The hybrid solution was prepared using zirconium propoxide and silver nitrate and stabilized through a low-temperature two-stage annealing protocol. The crystal structure of the coating was determined by XRD, and the presence of dense tetragonal ZrO₂ phase and crystalline Ag phases was confirmed. SEM-EDS analyses revealed a compact coating structure of approximately 1.8 μ m thickness with homogeneously distributed Ag nanoparticles on the surface. As a result of the electrochemical corrosion tests, it was determined that the open circuit potential shifted to more noble values, the corrosion current density decreased, and the corrosion rate decreased by more than 70% on the surfaces where the Ag/ZrO₂ coating was applied. In the tribological tests, a decrease in the coefficient of friction, narrowing of wear marks, and significant reduction in surface damage were observed in dry and physiological (HBSS) environments. The findings revealed that the Ag/ZrO₂ hybrid coating significantly improved the surface performance of the Ti45Nb alloy both mechanically and electrochemically and offers high potential for biomedical implant applications.

Keywords: Ag/ZrO₂ hybrid coating; Ti45Nb; corrosion test; tribological test; HBSS



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1. Introduction

Titanium and titanium-based alloys are widely preferred in orthopedic and dental implant designs due to their superior specific strength, biocompatibility, and high corrosion resistance [1,2]. In particular, β -type titanium alloys stabilized with biocompatible elements such as Nb, Ta, and Zr contribute to long-term implant stability by minimizing the stress shielding effect thanks to their elastic modulus values being close to those of bone tissue [3–5]. In this context, the Ti45Nb alloy stands out as a β -type titanium alloy that has attracted attention recently due to both its mechanical adequacy and biological performance, which are suitable for cell–tissue interaction [6]. However, the relatively low surface hardness and wear resistance of Ti-Nb based alloys constitute a limiting factor, especially in load-bearing implant areas [7,8]. In addition, corrosion occurring on the surface during long-term use in physiological environments threatens the structural integrity of the implant and increases the risk of inflammation in the surrounding tissues. Therefore, surface modifications that will improve both the tribological and corrosion properties and also have biocompatible and functional properties are of critical importance [9,10]. In this regard, ceramic-based coatings have been developed to increase the implant performance through

surface modification based on phases such as zirconium dioxide (ZrO_2), which stands out with properties such as high hardness, chemical stability, and biocompatibility [11]. These superior physicochemical properties of ZrO_2 provide significant advantages in terms of long-term implant stability and resistance to surface wear. In addition, the addition of silver (Ag) not only provides antimicrobial activity to the coating system, but also improves the tribological performance through morphological modifications at the microstructural level [12,13]. In addition to the β -type Ti45Nb alloy, various titanium-based surfaces have been systematically investigated in terms of their tribological behavior. For instance, it has been shown that the phase composition of titanium alloys plays a critical role in determining their wear mechanisms and frictional stability. A comparative study on α (T50), $\alpha + \beta$ (Ti-6Al-4V), and β (Ti-5553) titanium alloys under steel ball contact revealed that different oxide phases form during sliding, governing distinct wear regimes. While β -type Ti-5553 exhibited a single abrasive stage dominated by the formation of TiO_2 -anatase, the α and $\alpha + \beta$ alloys transitioned to additional regimes involving TiO_2 -rutile and Fe-oxide layers, which led to fluctuations in the coefficient of friction and wear severity [14]. Li et al. [15] reported that uncoated β -Ti exhibited severe adhesive wear in dry contact due to its low surface hardness, whereas surface nitriding significantly improved the wear resistance. Similarly, Yilmazer et al. [16] demonstrated that Ti-Nb-Zr substrates coated with TiO_2 showed a reduced wear track width and lower coefficient of friction compared with uncoated alloys. Moreover, recent studies by Frutos et al. [4] and Çomaklı et al. [17] showed that oxide, nitride, and bioceramic coatings enhanced the tribocorrosion behavior of β -type Ti alloys, but often lacked antibacterial functionality. These findings highlight the need for hybrid coating strategies that offer both mechanical durability and biological compatibility. In addition to mechanical and electrochemical stability, lubrication is a crucial tribological parameter in biomedical implants, especially in synovial joint environments where surface interactions with biological fluids significantly influence the wear mechanisms. The wettability and lubrication behavior of implant surfaces directly affect the formation and stability of boundary layers, which in turn co-determine the friction and wear performance. Recent studies have emphasized the importance of mimicking the physiological lubrication conditions during in vitro assessments. For instance, Peta et al. investigated the lubrication behavior of electro-discharge machined titanium implant surfaces using artificial synovial fluid and demonstrated that microtextured surface features and discharge energy significantly influenced the contact angle and surface free energy, thereby affecting the lubrication regimes and frictional response [18]. Although there have been some preliminary studies on the potential applications of Ag/ ZrO_2 hybrid coatings in biomedical fields in the current literature, studies that have addressed the effects of such coatings on β -type Ti alloys in a multifaceted and systematic manner are extremely limited. Alagarsamy et al. reported that coated Ti surfaces exhibited better a biomechanical performance and were more resistant to surface damage compared with uncoated surfaces due to the nanostructured grains formed on the surface morphology of the Ag-doped ZrO_2 coatings [19]. Kaliyaperumal et al. synthesized Ag/ ZrO_2 nanocomposites by the hydrothermal method, and as a result of the antimicrobial tests, it was determined that ZrO_2 nanocomposites containing 10% Ag exhibited significant biocidal activity against *E. coli*, *S. aureus*, *A. niger*, and *C. albicans* and formed a wider inhibition zone compared with pure AgO and ZrO_2 . These results reveal that Ag/ ZrO_2 systems have strong antimicrobial potential [20]. Sredojević et al. [21] evaluated the antibacterial activity and cytotoxic effect of Ag nanoparticles deposited in situ on dihydroquercetin (DHQ) functionalized ZrO_2 nanoparticles synthesized by the sol-gel method. The obtained hybrid system showed strong antibacterial activity against *E. coli* and *S. aureus* bacteria. In particular, considering the previous studies conducted, the lack of comprehensive studies evaluating

the tribological behavior from a holistic perspective, together with the electrochemical corrosion properties, both in dry and simulated physiological environment conditions, is striking. This absence indicates an important research gap in determining the place of biocompatible hybrid coatings in advanced implant designs. Based on this deficiency, in the present study, a Ag/ZrO₂ hybrid coating was applied on a biocompatible β -type Ti45Nb alloy by the spin coating method, and the microstructural properties of this coating, such as the crystal structure, surface morphology, surface hardness and surface roughness as well as tribological behavior and electrochemical corrosion performance in dry and simulated physiological conditions, were evaluated in a multifaceted manner. The hybrid solution prepared by the sol–gel method was stabilized by a two-stage annealing protocol at low temperature to provide tetragonal phase formation in the ZrO₂ matrix and the controlled distribution of Ag phase on the surface was the aim.

2. Materials and Methods

2.1. Material and Hybrid Solution Preparation

In this study, a commercially available Ti45Nb alloy (15 mm × 15 mm × 2 mm) was used as the base material. The Ti45Nb alloy utilized in this study primarily consisted of titanium and niobium, with an atomic composition of approximately 69.22 at. % Ti and 30.16 at. % Nb, alongside trace amounts of other elemental constituents [22]. The polished surfaces were cleaned and dried in an ultrasonic bath with acetone, ethanol, and distilled water for 5 min, respectively. The coating solution (Ag/ZrO₂ hybrid solution) was prepared by a modified sol–gel method. Zirconium(IV) propoxide (Zr(OC₃H₇)₄, in 70% isopropanol, Sigma-Aldrich, St. Louis, MO, USA) was used as the zirconium source, and silver nitrate (AgNO₃, Merck, Rahway, NJ, USA) was used as the silver source. A total of 1 mmol Zr (OC₃H₇)₄ was mixed with 10 mL of absolute ethanol under a nitrogen atmosphere for 30 min in a reaction vessel. Then, 2 mL of the ethanol solution containing 0.5 mmol AgNO₃ was added dropwise. Next, 0.1 mL of acetic acid and 0.05 mL of distilled water were added to initiate hydrolysis. The mixture was stirred on a magnetic stirrer for 2 h until a homogeneous solution was obtained. The solution components and molar ratios used were determined based on experience gained from previous sol–gel studies on Ag/ZrO₂ hybrid systems in the literature. In particular, a ratio of 1 mmol Zr (OC₃H₇)₄ and 0.5 mmol AgNO₃ (Zr:Ag = 2:1) has been reported to ensure a homogeneous dispersion of silver nanoparticles in solution while preventing excessive agglomeration and uncontrolled precipitation [19,23]. Furthermore, the amounts of acetic acid and water used in the hydroxylation step (0.1 mL and 0.05 mL, respectively) were optimized for controlled hydrolysis of the Zr precursor and stable formation of the gel structure [20]. These content parameters were chosen in accordance with preliminary experiments to support the surface integrity, particle distribution, and phase stabilization during film formation. Thus, both the tetragonal phase formation of ZrO₂ and the controlled surface migration of the Ag phase were achieved.

2.2. Spin Coating Process

The prepared Ag/ZrO₂ solution was coated on Ti45Nb substrates using a programmable spin coater. Each sample was coated by spinning at 3000 rpm for 30 s, and this process was repeated for three layers. After each layer, the samples were subjected to a 5 min pre-bake process at 100 °C to ensure evaporation of the solvent and partial densification of the layer. After coating, a two-stage annealing protocol was applied to ensure crystallization of the hybrid film and to promote the controlled formation of Ag nanoparticles. In the first step, the samples were annealed at 300 °C for 1 h (temperature increase rate: 2 °C/min), then at 450 °C for 30 min in an air atmosphere. This method provides

tetragonal phase stabilization in the ZrO_2 matrix and controls the migration of the Ag phase to the surface. To ensure optimal film quality and functional performance, the spin coating parameters were systematically optimized through a set of preliminary trials. Various spin speeds (1000–4000 rpm), coating cycles (1–5 layers), and pre-baking durations (3–10 min at 80–120 °C) were evaluated to identify the conditions that provided the most uniform, crack-free, and adherent coatings. The final parameters (3000 rpm spin speed, 3-cycle coating, and 5-min pre-baking at 100 °C) were selected based on the resulting film's morphological consistency, XRD crystallinity, and SEM-EDS surface integrity. Furthermore, the dual-step annealing protocol (300 °C/1 h and 450 °C/30 min) was specifically implemented to induce the tetragonal phase stabilization of ZrO_2 and to facilitate Ag nanoparticle segregation toward the surface, thereby enhancing the hybrid coating functionality. These optimization steps ensured that the final coating possessed a dense microstructure, enhanced adhesion, and reproducible electrochemical and tribological performance.

2.3. Coating Characterization

The morphological analysis and elemental distributions of the coated surfaces were determined by a field emission scanning electron microscope (FEI Quanta FEG-450, Thermo Fisher Scientific, Waltham, MA, USA) and energy dispersive X-ray spectroscopy (EDS; FEI QUANTA 250, Thermo Fisher Scientific, USA). Crystal structures were analyzed by X-ray diffraction (Empyrean XRD system, Malvern Panalytical, Almelo, The Netherlands) scanning in the range of 20–90° (2 θ) using a $\text{Cu-K}\alpha$ beam ($\lambda = 1.5406 \text{ \AA}$). In addition, the surface hardness of the samples was determined using a universal mechanical tester (UMT-2, Bruker Corporation, Billerica, MA, USA) that allowed for the high accuracy assessment of mechanical performance at the micro scale. Average Vickers hardness values were calculated by taking measurements from at least five randomly selected points on each sample. The measurements were performed with high repeatability thanks to the precise load application and positioning features of the device. The surface roughness measurements were performed using a Bruker Contour GT-I 3D optical profilometer (Contour GT-I, Bruker, USA) operating in vertical scanning interferometry (VSI) mode, which provides a vertical resolution of 0.01 nm and a lateral resolution of 0.2 μm under the selected scanning parameters. Area-based scans were acquired using a 5 $\times$ objective lens over a 500 $\mu\text{m} \times 500 \mu\text{m}$ region. To ensure statistical robustness and repeatability, each sample surface was scanned at five randomly selected locations, with three repeated scans per region. The reported R_a values represent the mean $\pm$ standard deviation across these measurements. In order to evaluate the electrochemical resistance of the Ag/ ZrO_2 hybrid coating under physiological and inflammatory conditions, corrosion tests were performed in Hanks' Balanced Salt Solution (HBSS). The composition of Hanks' Balanced Salt Solution (HBSS) is given in Table 1. The electrochemical corrosion analyses were conducted with open circuit potential (OCP) and potentiodynamic polarization measurements. Measurements were performed in a GAMRY Reference 3000 Potentiostat/Galvanostat/ZRA (Gamry Instruments, Warminster, PA, USA) using a three-electrode cell system at a constant temperature of 37 °C; Ag/AgCl was used as the reference electrode and a graft rod was used as the counter electrode. The uncoated Ti45Nb and Ag/ ZrO_2 coated Ti45Nb samples were used as working electrodes, and the open surface area was limited to 1 cm^2 . Potentiodynamic polarization (PDP) tests were performed between -0.25 V (below OCP) and $+1.0 \text{ V}$ (above OCP) at a scanning rate of 1 mV/s. The OCP measurements were performed with a 5400 s stabilization period. In order to evaluate the tribological performance of the uncoated and Ag/ ZrO_2 hybrid coated Ti45Nb alloys, wear tests were performed using the Bruker UMT-2 multifunctional mechanical testing system. Experimental studies were conducted at room temperature ($23 \pm 2 \text{ °C}$) under atmospheric pressure. The tribological tests were conducted using a “ball-

on-flat” reciprocating motion configuration on a Bruker UMT-2 multifunctional mechanical tester. A normal load of 2 N was applied, with a stroke length of 5 mm and a reciprocating frequency of 1 Hz, over a total of 1000 cycles, corresponding to an approximate sliding distance of 100 mm. Tests were performed at ambient temperature (23 ± 2 °C) under two different environmental conditions: dry friction and Hanks’ Balanced Salt Solution (HBSS) to simulate the physiological conditions. All test parameters were kept constant and standardized across the samples to ensure comparability. Throughout the tests, the coefficient of friction (COF) was continuously recorded in real-time. After testing, the width of the wear scars was analyzed using scanning electron microscopy (SEM), and the wear volume and wear rate were calculated in accordance with the ASTM G133 standard [24]. An Al_2O_3 (alumina) ball with a diameter of 6 mm was used as the counter surface. Al_2O_3 was selected due to its chemical inertness, high hardness, and dimensional stability, which allow for highly reproducible and controlled testing conditions. Although Al_2O_3 does not replicate the mechanical behavior of bone or cartilage, it is routinely employed in standardized tribological protocols, such as ASTM G133, to simulate severe yet consistent wear scenarios that facilitate a comparative evaluation of surface performance. Moreover, alumina-based ceramics have been utilized in various implant systems, including ceramic-on-metal and ceramic-on-polymer couples, underscoring their relevance in preclinical wear assessments of biomedical materials [25]. All characterization measurements (hardness, roughness, electrochemical tests, and wear tests) were repeated three times, and each value presented is the average of three independent replicates.

Table 1. The composition of Hanks’ Balanced Salt Solution. Reprinted from Ref. [26].

Component	Concentration (mM)
NaCl	137.93
KCl	5.36
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	1.26
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	0.81
Na_2HPO_4	0.34
KH_2PO_4	0.44
NaHCO_3	4.17
Glucose	5.55

3. Results and Discussion

3.1. Surface Analysis

The phase analyses of the Ag/ ZrO_2 hybrid coating applied on the Ti45Nb alloy by the sol–gel method were characterized by the X-ray diffraction (XRD) technique. In the XRD graph presented in Figure 1, characteristic reflections specific to the β phase of the uncoated Ti45Nb alloy were observed clearly. In the uncoated sample, reflections corresponding to the (110), (200), and (211) planes at the approximately $2\theta \approx 38.5^\circ$, 55.7° , and 69.0° positions, respectively, were observed to form the body-centered cubic (BCC) crystal structure of β -TiNb alloy. In the XRD graph obtained after coating, characteristic peaks belonging to new phases were observed in addition to the peaks coming from the Ti45Nb base material. The angle of approximately $2\theta \approx 28.2^\circ$ was associated with the (111) planes of the monoclinic ZrO_2 phase [JCPDS 37-1484], while the peaks observed around 30.2° , 35.2° , 50.2° , and 60.0° corresponded to the (101), (110), (112), and (211) planes of the tetragonal ZrO_2 phase [JCPDS 80-0965], respectively. These findings revealed that the crystal structure of the ZrO_2 coating applied by the sol–gel method contained dense tetragonal phases [27]. In addition, the observation of reflections belonging to Ag (111), Ag (200), Ag (220), and Ag (311) planes at approximately $2\theta \approx 38.1^\circ$, 44.3° , 64.4° , and 77.4° angles, respectively, confirmed that

silver had precipitated as crystalline in the coating and was among the phases detectable by XRD. This supports that the Ag nanoparticles had successfully dispersed into the ZrO₂ matrix, and the structure exhibited a multiphase character [28].

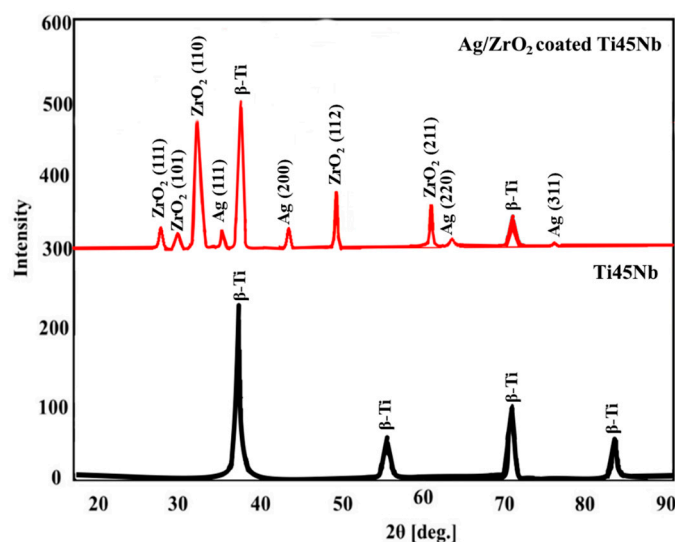


Figure 1. XRD patterns of the Ag/ZrO₂ hybrid coating on the Ti45Nb alloy.

The surface and cross-sectional morphologies of the Ag/ZrO₂ hybrid coating applied to the Ti45Nb alloy by the spin coating method were examined by scanning electron microscope (SEM) and are shown in Figure 2. In the surface image given in Figure 2a, granular particles distributed homogeneously throughout the film were observed. These particles, with a diameter of approximately 100–200 nm, were considered to be Ag nanoparticles dispersed in the ZrO₂ matrix phase. No cracks, peeling, or obvious micropores were observed on the surface. The cross-sectional SEM image presented in Figure 2b revealed that the coating was bonded to the substrate in a compatible manner and its average thickness was approximately 1.8 µm. The film had a compact and discontinuity-free structure obtained after the multilayer spin coating process. This structural integrity is related to the gradual densification and crystallization of the film as a result of pre-baking (100 °C/5 min) and double-stage annealing (300 °C/1 h + 450 °C/30 min). In addition, the mobility of Ag ions increased during the high-temperature annealing process, which may have promoted the formation of Ag nanoparticles on the surface. In order to evaluate the mechanical and superficial effects of the Ag/ZrO₂ hybrid coating on the Ti45Nb alloy, Vickers microhardness and surface roughness (Ra) measurements were carried out, the results of which are given in Table 2. The uncoated Ti45Nb alloy showed a microhardness value range of 200 ± 0.2 Vickers units on the HV0.1 scale. These values confirm the low hardness structure of the alloy due to its β phase character. After the application of the Ag/ZrO₂ hybrid coating, it was observed that the hardness value showed a significant increase, reaching 390 ± 0.4 HV. The hybrid film with a thickness of approximately 1.8 ± 0.09 µm provided this increase by creating a barrier with high hardness on the surface. This can be attributed to the ceramic structure and high crystallinity of ZrO₂, while it is thought that the Ag phase in the coating increases the microstructural density by filling the microvoids. In the surface roughness measurements, the uncoated Ti45Nb alloy exhibited a fairly smooth surface in the range of Ra ≈ 0.09 ± 0.01 µm. In contrast, it was observed that the roughness value in the Ag/ZrO₂ coated samples increased to the level of 0.18 ± 0.02 µm. This increase was due to the granular microstructure that formed during the coating and the micro-protrusions formed by the Ag nanoparticles embedded in the surface. As a result, the applied Ag/ZrO₂ hybrid coating contributed to the mechanical performance by increasing the surface hard-

ness and increased the surface roughness in a controlled manner. The increase in surface hardness observed following the Ag/ZrO₂ hybrid coating was largely due to the high structural hardness of the ZrO₂ ceramic phase, which was dominant in the coating. In particular, the tetragonal phase, stabilized at low temperatures, provides high resistance to plastic deformation and increases the mechanical strength of the surface [27]. Additionally, it was estimated that the silver nanoparticles within the coating increased the microdensity by filling intergranular micropores within the microstructure, thus contributing to the structural integrity. The resulting compact, multiphase film structure limits the propagation of cracks that may occur under applied mechanical loads and ensures that the surface exhibits crack-resistant behavior [23].

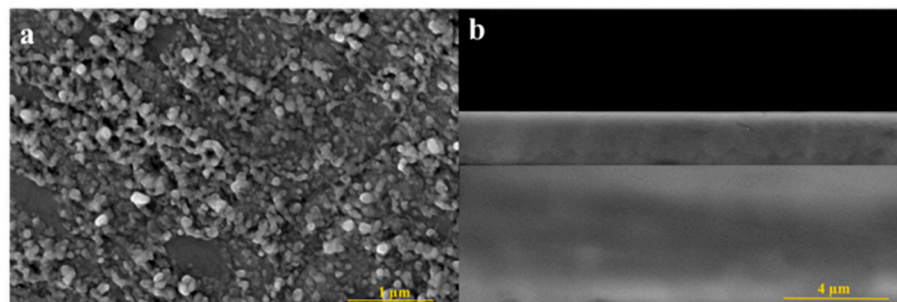


Figure 2. (a) The surface SEM and (b) the cross-section SEM images of the Ag/ZrO₂ hybrid coating on the Ti45Nb alloy.

Table 2. The Ti45Nb alloy and Ag/ZrO₂ hybrid coated Ti45Nb alloy sample: thickness, average surface roughness, and hardness values.

Samples	Coating Thickness (μm)	Hardness Value (HV _{0.1})	Roughness Value (R _a -μm)
Uncoated Ti45Nb	-	200 ± 0.2	0.09 ± 0.01
Ag/ZrO ₂ coated Ti45Nb	1.8 ± 0.09	390 ± 0.4	0.18 ± 0.02

The chemical composition of the coating was determined by energy dispersive X-ray spectroscopy (EDS) analysis, as given in Figure 3. As a result of the analysis, it was determined that there were three main elements in the coating layer: zirconium (Zr) 34.85%, oxygen (O) 47.73%, and silver (Ag) 17.42% (by atomic weight). These ratios confirmed that the main component of the coating was the ZrO₂ matrix phase and that the Ag additive was successfully integrated. In particular, the strong and intense signals of the Zr and O elements indicated that the ZrO₂ structure formed stably, while the presence of Ag signals revealed that metallic Ag nanoparticles accumulated locally on the surface and reached a level that could be easily detected by EDS. No significant signal belonging to the Ti and Nb elements was observed in the EDS spectrum, which shows that the approximately 1.5 μm thick coating obtained by spin coating exceeded the analytical depth of the EDS and minimized the substrate effect. This is further evidence that the coating formed compactly and with sufficient thickness on the surface.

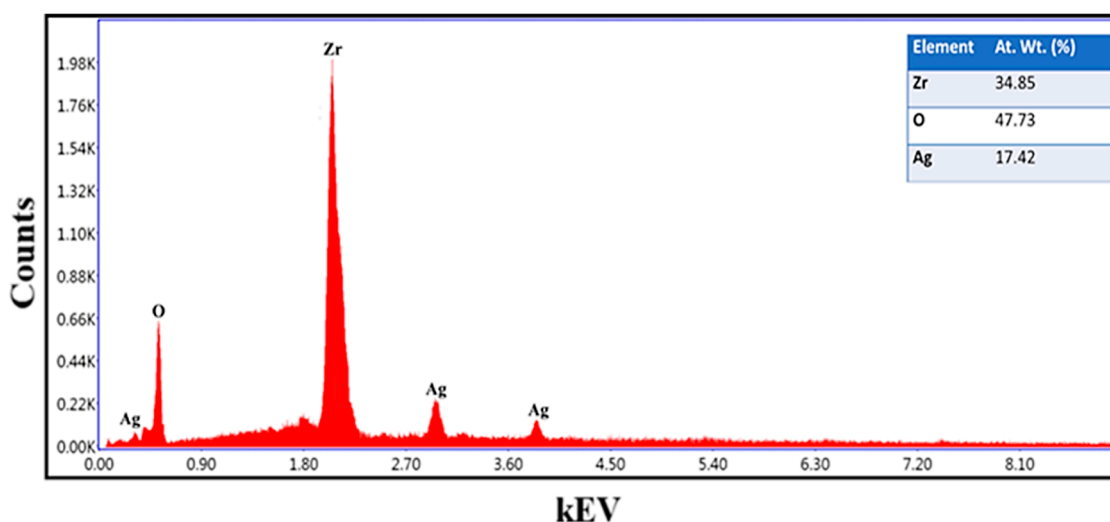


Figure 3. EDS results of the Ag/ZrO₂ hybrid coating on the Ti45Nb alloy.

3.2. Electrochemical Corrosion Analyses

The OCP and PDP curves obtained as a result of the electrochemical corrosion tests are given in Figure 4 and Table 3. Figure 4a shows the OCP curves of the uncoated and Ag/ZrO₂ hybrid coated Ti45Nb alloy. While the open circuit potential value was measured as approximately -0.35 V in the uncoated Ti45Nb sample, this value increased to -0.16 V after the coating. This shows that the coating exhibited a more noble behavior and supported the formation of the passive film. The PDP curves obtained from the potentiodynamic polarization tests performed to evaluate the effect of Ag/ZrO₂ hybrid coating on the corrosion resistance of the Ti45Nb alloy are presented in Figure 4b. Compared with the uncoated Ti45Nb alloy, the Ag/ZrO₂ hybrid coating led to a notable improvement in corrosion resistance, as evidenced by a positive shift in the corrosion potential (E_{corr}) from -0.35 V to -0.16 V and a significant decrease in the corrosion current density (I_{corr}) from 1.53×10^{-5} mA/cm² to 4.94×10^{-6} mA/cm². These findings indicate that the coating significantly slowed down the kinetics of the corrosion reactions and promoted the formation of the passive layer. The increase in the cathodic Tafel slope coefficient (β_c) from 240 mV/dec to 360 mV/dec in the Ag/ZrO₂ coated sample indicates that the reduction reactions occurred in a more controlled manner and the surface became more resistant to electrochemical processes such as oxygen reduction due to the coating. On the other hand, the decrease in the anodic Tafel slope (β_a) from 145 mV/dec to 128 mV/dec suggests an enhanced passivation behavior and indicates that the anodic reactions proceeded in a more stable and controlled manner. When evaluated in terms of the corrosion rate, the 5.56 mpy value measured in the uncoated Ti45Nb alloy decreased to 1.48 mpy after the Ag/ZrO₂ coating, providing an improvement of approximately 73%. This improvement shows that the coating prevented the diffusion of aggressive ions with its physical barrier effect and formed a more stable oxide/hydroxide layer on the surface. These results show that the Ag/ZrO₂ hybrid coating significantly increased the corrosion resistance in the Hanks' Balanced Salt Solution when applied to the Ti45Nb alloy and increases its potential for use as a biomaterial. This increase in corrosion resistance can be explained by the combined effects of both physical and electrochemical mechanisms. In the Ag/ZrO₂-coated samples, the dense ZrO₂ matrix formed an effective physical barrier against chloride and oxygen ion ingress, preventing the initiation of corrosion reactions. At the same time, silver particles within the coating could improve the passivation behavior by regulating electron exchange at the surface. The high cathodic Tafel slope coefficient in the coated samples confirmed that oxygen reduction reactions were suppressed and a more stable passive

film was formed. These results demonstrate that the coating not only provides physical protection, but also positively contributes to electrochemical processes [28,29].

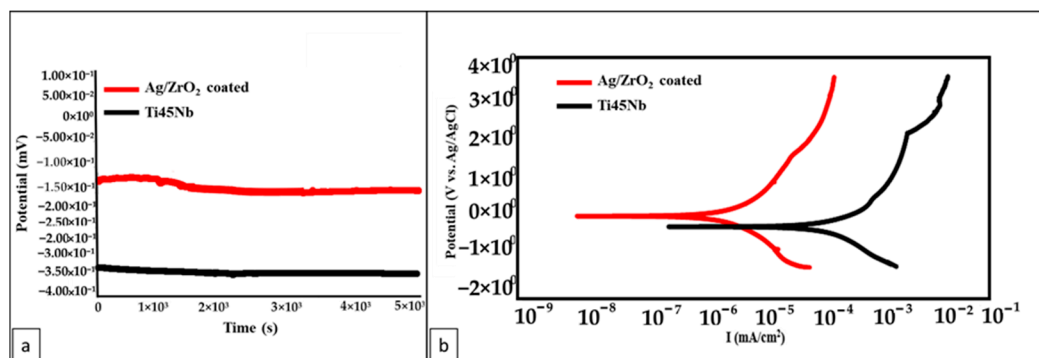


Figure 4. The uncoated and Ag/ZrO₂-coated Ti45Nb alloy in Hanks' Balanced Salt Solution (HBSS). (a) Open circuit potential (OCP) curves; (b) Potentiodynamic polarization curves.

Table 3. Potentiodynamic polarization test results of the uncoated and Ag/ZrO₂ hybrid coated Ti45Nb in Hanks' Balanced Salt Solution.

Material	E _{corr} (V)	I _{corr} (mA/cm ²)	β _a (mV/dec)	β _c (mV/dec)	Corrosion Rate (mpy)
Uncoated Ti45Nb	−0.35	1.53 × 10 ^{−5}	145	240	5.56
Ag/ZrO ₂ hybrid coated Ti45Nb	−0.16	4.94 × 10 ^{−6}	128	360	1.48

The uncoated and Ag/ZrO₂ coated Ti45Nb samples were analyzed by EDS after the electrochemical corrosion test in the HBSS environment, and the results are presented in Table 4. In the uncoated Ti45Nb alloy, mainly titanium (39.51% at.) and niobium (7.03% at.) elements were detected on the surface. Although these values are consistent with the composition of the alloy, these were observed at low levels due to oxidation on the surface and the limited depth perception of EDS analysis. The oxygen ratio, reaching a high value of 49.56%, indicated that a thick passive oxide layer (TiO₂ and Nb₂O₅) formed on the surface. In addition, the presence of calcium (2.25% at.) and phosphorus (1.65% at.) elements indicated the ionic adsorption or formation of calcium phosphate compounds on the surface. A significant difference was observed on the surface of the Ag/ZrO₂ coated Ti45Nb samples as a result of EDS analysis after corrosion. Dominantly, zirconium (31.75% at.), oxygen (53.40% at.), and silver (10.45% at.) elements were detected in the coating layer. The high oxygen content can be attributed to the presence of the zirconia matrix and surface oxidation in the physiological environment. Despite the electrochemical corrosion test, the observation of Ag content showed that silver was stably present in the coating matrix, and partial Ag⁺ ion release as well as antimicrobial functionality could be sustained. In addition, the presence of calcium (2.54% at.) and phosphorus (1.96% at.) elements on the coated surface revealed that the surface could exhibit biological activity by allowing Ca–P accumulation. The fact that titanium and niobium elements could not be detected in the coated sample confirmed that the coating completely covered the substrate and prevented direct contact with the corrosive environment. This structural integrity is consistent with the improved corrosion resistance previously demonstrated in polarization tests [29]. These findings indicate that the Ag/ZrO₂ hybrid coating will not only enhance corrosion resistance by acting as a physical barrier, but will also provide a favorable surface response in terms of biological integration by promoting Ca–P adsorption on the surface.

Table 4. EDS analysis of the corroded surfaces of the uncoated and coated Ti45Nb surfaces in Hanks' Balanced Salt Solution.

	Zr	O	Ag	Ca	P	Ti	Nb
Uncoated Ti45Nb (at.%)	-	49.56	-	2.25	1.65	39.51	7.03
Ag/ZrO ₂ coated Ti45Nb (at.%)	31.75	53.40	10.45	2.54	1.96	-	-

3.3. Tribological Properties

In Figure 5, the coefficient of friction (COF)–time graphs of the uncoated and Ag/ZrO₂ coated Ti45Nb alloys in a dry environment (Figure 5a,b) and HBSS environment (Figure 5c,d) under a 2 N normal load are presented. The uncoated Ti45Nb sample exhibited high-frequency fluctuations with an average COF value of approximately 0.32 ± 0.04 when tested in the dry environment (Figure 5a). This wavy profile indicates that microcracks formed on the surface, plastic deformation, and possible adhesion-wear mechanisms. This situation may be due to Ti45Nb not being able to form a stable tribological film during contact with the opposite surface due to its low surface hardness. Although the Ag/ZrO₂ coated sample exhibited a similar level of friction with a COF value of approximately 0.34 ± 0.05 in the dry environment (Figure 5b), less oscillations in the COF curve indicate that a more stable contact was provided at the tribological interface. This behavior suggests that the hybrid coating provides a more controlled and uniform contact surface during wear, and the surface topography of the coating suppresses sudden COF increases by distributing the tribological load. In the wear tests performed in the HBSS environment, the uncoated Ti45Nb sample (Figure 5c) showed lower friction with an average COF value of 0.22 ± 0.04 compared with the dry environment. This decrease can be explained by the physiological solution creating a boundary lubricant environment between the surfaces and reducing the microadhesion effects. However, the continuously increasing COF trend observed in the curve indicates that the passive layer that forms on the surface deteriorates over time and tribocorrosion effects damage the surface. The Ag/ZrO₂ coated sample in the HBSS environment (Figure 5d) exhibited a lower oscillation amplitude and a more stable tribological response despite an average COF value of 0.27 ± 0.03 (Table 5). This stability can be associated with the resistance of the coating surface to corrosion and the tendency of the Ag/ZrO₂ structure to form a tribochemically passive and protective film. At the same time, the potential solid lubricant effect of Ag may also support this stability. As a result, the Ag/ZrO₂ coating significantly improved the tribological performance by making the friction behavior more predictable in both the dry and HBSS environments.

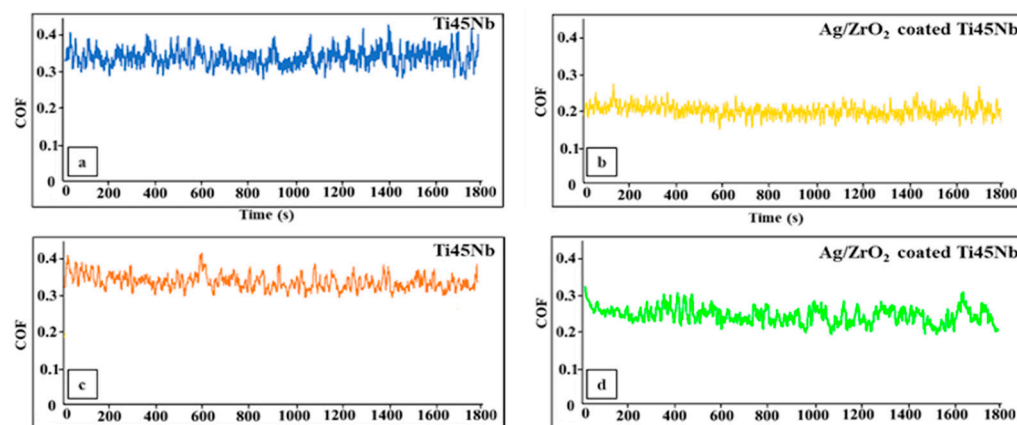
**Figure 5.** COF graphs obtained after wear tests (a,b) in the dry and (c,d) in HBSS environments.

Table 5. Average coefficient of friction and wear rate values of the uncoated and Ag/ZrO₂-coated Ti45Nb samples tested under a 2 N wear load in dry and HBSS environments.

Parameters	Average Coefficient of Friction (μ)		Average Wear Rate ($\times 10^{-6}$ mm ³ /Nm)	
	DRY	HBSS	DRY	HBSS
Uncoated Ti45Nb	0.32 $\pm$ 0.04	0.22 $\pm$ 0.04	1.12 $\pm$ 0.04	0.85 $\pm$ 0.04
Ag/ZrO ₂ coated Ti45Nb	0.34 $\pm$ 0.05	0.27 $\pm$ 0.03	0.91 $\pm$ 0.03	0.78 $\pm$ 0.02

Figure 6 presents the SEM images obtained after the wear tests performed in dry and HBSS environments on the uncoated and Ag/ZrO₂ hybrid coated surfaces of the Ti45Nb alloy. In Figure 6a, in the approximately 1000 μ m wide wear track formed on the surface of the uncoated Ti45Nb alloy after the wear test performed in the dry environment, distinct parallel scratches, deformation zones, and flattened areas due to microplastic on the surface were observed. This situation shows that the adhesion mechanism due to surface deformation is effective together on the surface of the material. An insufficient surface hardness and low surface strength increase the size of these tracks and can easily lead to mechanical damage to the surface [30]. In the SEM image of the Ti45Nb alloy with the Ag/ZrO₂ coating applied in Figure 6b after dry environment wear, the width of the wear track was approximately 760 μ m, and a significantly narrower track was formed compared with the uncoated surface. A more uniform and less damaged wear area was observed, with reduced scratch density on the surface. This indicates that the coating limited the adhesion effects by increasing the surface hardness [19]. In addition, it was seen that the tribological performance improved due to the high hardness of the ZrO₂ ceramic and the friction-reducing effect of Ag. In Figure 6c, the wear track image of the uncoated Ti45Nb alloy after the wear test in HBSS solution is given. It is noteworthy that the wear track, which was approximately 260 μ m wide, was narrower than in the dry environment. This narrowing can be explained by the fact that the HBSS environment partially reduces friction with the liquid film effect and limits wear to some extent [31]. However, irregular scratches, tears, and local accumulations on the surface indicate that the adhesion wear mechanism continues and the passivation effect does not provide full protection. In Figure 6d, the narrowest wear zone was observed in the wear track with an approximately 220 μ m width formed after abrasion of the Ag/ZrO₂ coated Ti45Nb alloy in the HBSS environment. The coating layer significantly increased the wear resistance thanks to both its mechanical strength and chemical stability [32]. It was observed that the scratches on the surface were limited, a more homogeneous structure could be maintained, and there were micro-level flaking tracks in places. These results reveal that the hybrid coating provided effective protection in both the dry and physiological environments and that the surface gained resistance against wear mechanisms. In general, the reduction in the width of the wear tracks observed on the sample surfaces after the application of the Ag/ZrO₂ hybrid coating indicates that the coating provides effective mechanical reinforcement and chemical stability against corrosion degradation. Additionally, the presence of HBSS as a testing medium contributed to a further reduction in wear severity due to the lubricating effect of the liquid film, which diminishes direct asperity contact. From a mechanistic perspective, adhesive wear was identified as the predominant mechanism on the uncoated Ti45Nb surfaces, characterized by severe material transfer and ploughing. However, on the coated surfaces, this wear mechanism was significantly mitigated. Instead, a combination of mild adhesive interaction and the presence of a protective film, attributed to the Ag/ZrO₂ layer, played a key role in minimizing wear damage. The contribution of the Ag/ZrO₂ hybrid coating to tribological performance can be explained by both physical surface modification and tribochemical interactions. The highly crystalline ceramic nature of ZrO₂ enables the surface

to resist plastic deformation and limits surface depressions that may occur during wear. Especially in HBSS media, this hybrid structure increases the stability of a tribochemically formed passive layer on the surface, and this layer creates a barrier against both mechanical frictional effects and tribocorrosion processes induced by corrosive ions [29,33]. As a result of these synergistic mechanisms, lower friction coefficients, narrower wear scars, and more predictable surface behavior can be achieved in both dry and physiological environments.

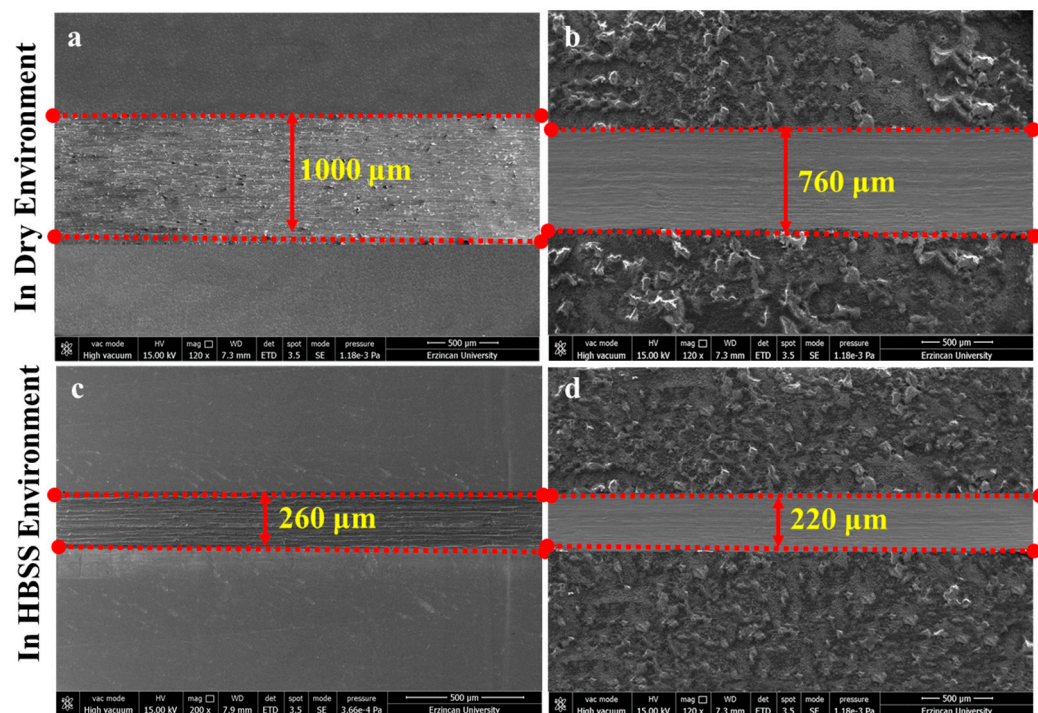


Figure 6. SEM images of the samples after wear treatment (a) uncoated, (b) Ag/ZrO₂-coated Ti45Nb alloy in dry environment; (c) uncoated and (d) Ag/ZrO₂-coated Ti45Nb alloy in the HBSS environment.

4. Conclusions

In general, the XRD analysis results revealed that the Ag/ZrO₂ hybrid coating applied on the Ti45Nb alloy was crystalline in character, ZrO₂ was densely present in the tetragonal phase, and Ag crystallized as a separate phase. The coating surface contained homogeneously distributed Ag nanoparticles. Granular structures of approximately 100–200 nm in size were observed on the surface in the SEM analyses; it was determined that these structures were Ag nanoparticles dispersed in the ZrO₂ matrix. The Ag/ZrO₂ coating significantly increased the surface hardness of the Ti45Nb alloy. While the Vickers microhardness value was 180–220 HV on the uncoated surface, this value increased to 370–410 HV after coating. The potentiodynamic polarization results clearly demonstrated the enhanced corrosion resistance of the Ag/ZrO₂ hybrid coating on the Ti45Nb alloy. The significant reduction in corrosion rate from 7.56 mpy (uncoated) to 1.48 mpy after coating confirmed the effectiveness of the Ag/ZrO₂ layer as a protective barrier, significantly suppressing electrochemical degradation and enhancing surface passivation. EDS analyses showed that the coating maintained its integrity after corrosion. In addition, wear tests performed revealed that the Ag/ZrO₂ coating improved the tribological behavior in both dry and physiological environments. The friction coefficient of the uncoated surface was measured as 0.32 ± 0.04 in the dry environment and 0.22 ± 0.04 in the HBSS environment, while these values were 0.34 ± 0.05 and 0.27 ± 0.03 after coating, respectively, providing a more stable friction behavior. According to the SEM images, the wear scar width decreased from $\approx 1000 \mu\text{m}$ to $\approx 760 \mu\text{m}$ in the dry environment and from $\approx 260 \mu\text{m}$ to $\approx 220 \mu\text{m}$ in the HBSS

environment with the application of the coating; this narrowing is related to the mechanical resistance provided by the coating against wear.

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References

- Hossain, N.; Islam, M.A.; Ahmed, M.M.S.; Chowdhury, M.A.; Mobarak, M.H.; Rahman, M.M.; Hossain, M.H. Advances and significances of titanium in dental implant applications. *Results Chem.* **2024**, *7*, 101394. [\[CrossRef\]](#)
- Siddiqi, A.; Payne, A.G.T.; De Silva, R.K.; Duncan, W.J. Titanium implants: An overview of clinical applications and complications. *J. Biomed. Mater. Res. Part B Appl. Biomater.* **2011**, *97*, 396–408.
- Sun, Y.; Liu, Q.; Yu, Z.; Ren, L.; Zhao, X.; Wang, J. Study on Osseointegration Capability of β -Type Ti-Nb-Zr-Ta-Si Alloy for Orthopedic Implants. *Materials* **2024**, *17*, 472. [\[CrossRef\]](#) [\[PubMed\]](#)
- Frutos, E.; Karlík, M.; Jiménez, J.A.; Langhansová, H.; Lieskovská, J.; Polcar, T. Development of new β/α'' -Ti-Nb-Zr biocompatible coating with low Young's modulus and high toughness for medical applications. *Mater. Des.* **2018**, *142*, 44–55. [\[CrossRef\]](#)
- Jawed, S.F.; Rabadia, C.D.; Liu, Y.J.; Wang, L.Q.; Li, Y.H.; Zhang, X.H.; Zhang, L.C. Beta-type Ti-Nb-Zr-Cr alloys with large plasticity and significant strain hardening. *Mater. Des.* **2019**, *181*, 108064. [\[CrossRef\]](#)
- Mohammed, M.T.; Khan, Z.A.; Siddiquee, A.N. Beta titanium alloys: The lowest elastic modulus for biomedical applications—A review. *Int. J. Chem. Mol. Nucl. Mater. Metall. Eng.* **2014**, *8*, 726–731.
- Yilmazer, H.; Niinomi, M.; Nakai, M.; Cho, K.; Hieda, J.; Todaka, Y.; Miyazaki, T. Mechanical properties of a medical β -type titanium alloy with specific microstructural evolution through high-pressure torsion. *Mater. Sci. Eng. C* **2013**, *33*, 2499–2507. [\[CrossRef\]](#) [\[PubMed\]](#)
- Bordbar-Khiabani, A.; Gasik, M. Electrochemical and Biological Characterization of Ti-Nb-Zr-Si Alloy for Orthopedic Applications. *Sci. Rep.* **2023**, *13*, 2312. [\[CrossRef\]](#) [\[PubMed\]](#)
- Szczęsny, G.; Kopec, M.; Kowalewski, Z.L. Toxicity, irritation, and allergy of metal implants: Historical perspective and modern solutions. *Coatings* **2025**, *15*, 361. [\[CrossRef\]](#)
- Li, Y.; Tian, P.; Cao, H.; Wang, Y.; Zhao, X.; Han, S.; Wang, C. Remarkable enhancement of corrosion resistance and tribological properties of chitosan-MXene based hydrogel coating on the surface of Ti6Al4V alloy. *Tribol. Int.* **2024**, *192*, 109229. [\[CrossRef\]](#)
- Srinivasan, G.; Manickam, A.; Sivakumar, S.; Murugan, J.; Elangomannan, S.; Mohan, S. A comprehensive review: Surface modification strategies to enhance corrosion resistance of zirconia-based biomaterials in implant applications. *J. Mater. Sci. Mater. Eng.* **2025**, *20*, 76. [\[CrossRef\]](#)
- Lee, M.; Han, S.I.; Kim, C.; Velumani, S.; Han, A.; Kassiba, A.H.; Castaneda, H. ZrO₂/ZnO/TiO₂ nanocomposite coatings on stainless steel for improved corrosion resistance, biocompatibility, and antimicrobial activity. *ACS Appl. Mater. Interfaces* **2022**, *14*, 13801–13811. [\[CrossRef\]](#) [\[PubMed\]](#)
- Ismail, R.; Arfaoui, J.; Ksibi, Z.; Ghorbel, A.; Delahay, G. Effect of the amount of Ag on the performance of Ag/Ce-ZrO₂ catalyst for the total oxidation of toluene. *J. Chem. Lett.* **2024**, *5*, 186–191.
- Sola, T.; Maurel, P.; Weiss, L.; Fleury, E.; Grosdidier, T. A Comprehensive Investigation of the Tribological Behaviour of α , $\alpha+\beta$, and β Titanium Alloys against a Steel Counterpart. *Wear* **2025**, *560*, 205595. [\[CrossRef\]](#)
- Li, P.; Ma, X.; Wang, D.; Zhang, H. Microstructural and Mechanical Properties of β -Type Ti-Nb-Sn Biomedical Alloys with Low Elastic Modulus. *Metals* **2019**, *9*, 712. [\[CrossRef\]](#)
- Yilmazer, H.; Niinomi, M.; Cho, K.; Nakai, M.; Hieda, J.; Sato, S.; Todaka, Y. Microstructural Evolution of Precipitation-Hardened β -Type Titanium Alloy through High-Pressure Torsion. *Acta Mater.* **2014**, *80*, 172–182. [\[CrossRef\]](#)
- Çomaklı, O.; Yazıcı, M.; Demir, M.; Yetim, A.F.; Çelik, A. Effect of Bilayer Numbers on Structural, Mechanical, Tribological and Corrosion Properties of TiO₂-SiO₂ Multilayer Film-Coated β -Type Ti45Nb Alloys. *Ceram. Int.* **2023**, *49*, 3007–3015. [\[CrossRef\]](#)
- Peta, K.; Bartkowiak, T.; Rybicki, M.; Galek, P.; Mendak, M.; Wieczorowski, M.; Brown, C.A. Scale-Dependent Wetting Behavior of Bioinspired Lubricants on Electrical Discharge Machined Ti6Al4V Surfaces. *Tribol. Int.* **2024**, *194*, 109562. [\[CrossRef\]](#)
- Alagarsamy, K.; Vishwakarma, V.; Kaliaraj, G.S.; Vasantha, N.C.; Samuel, S.J.R. Biological adhesion and electrochemical behavior of Ag-ZrO₂ bioceramic coatings for biomedical applications. *J. Adhes. Sci. Technol.* **2020**, *34*, 349–368. [\[CrossRef\]](#)
- Kaliyaperumal, R.; Nagaraj, K.; Poovan, V.K.; Sakthikumar, K.; Govindasamy, C.; Sivakumar, A.S. Hydrothermal implementation with zirconia: Synthesis, characterization and investigation of biocidal activity of Ag/ZrO₂ nanocomposites. *Z. Phys. Chem.* **2024**, *238*, 209–221. [\[CrossRef\]](#)

21. Sredojević, D.; Lazić, V.; Pirković, A.; Periša, J.; Murafa, N.; Spremo-Potparević, B.; Živković, L.; Topalović, D.; Zarubica, A.; Krivokuća, M.J.; et al. Toxicity of silver nanoparticles supported by surface-modified zirconium dioxide with dihydroquercetin. *Nanomaterials* **2022**, *12*, 3195. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Aslan Çakır, M. Investigations of the wettability and electrochemical corrosion behavior of Nb₂O₅ thin films on a Ti45Nb alloy. *J. Mater. Eng. Perform.* **2023**, *32*, 9198–9205. [\[CrossRef\]](#)
23. Venkatesham, M.; Ayodhya, D.; Madhusudhan, A.; Veerabhadram, G. Synthesis of stable silver nanoparticles using gum acacia as reducing and stabilizing agent and study of its microbial properties: A novel green approach. *Int. J. Green Nanotechnol.* **2012**, *4*, 199–206. [\[CrossRef\]](#)
24. ASTM G133-05; Standard Test Method for Linearly Reciprocating Ball-on-Flat Sliding Wear. ASTM International: West Conshohocken, PA, USA, 2005.
25. Murali, R.; Bonar, S.F.; Kirsh, G.; Walter, W.K.; Walter, W.L. Osteolysis in Third-Generation Alumina Ceramic-on-Ceramic Hip Bearings with Severe Impingement and Titanium Metallosis. *J. Arthroplast.* **2008**, *23*, 1240.e13–1240.e19. [\[CrossRef\]](#) [\[PubMed\]](#)
26. Tonna, C.; Wang, C.; Mei, D.; Lamaka, S.V.; Zheludkevich, M.L.; Buhagiar, J. Biodegradation behaviour of Fe-based alloys in Hanks' balanced salt solutions: Part I. material characterisation and corrosion testing. *Bioact. Mater.* **2022**, *7*, 426–440. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Basahel, S.N.; Ali, T.T.; Mokhtar, M.; Narasimharao, K. Influence of crystal structure of nanosized ZrO₂ on photocatalytic degradation of methyl orange. *Nanoscale Res. Lett.* **2015**, *10*, 73. [\[CrossRef\]](#) [\[PubMed\]](#)
28. Chen, D.; Mei, D.; Li, Y.; Chen, L.; Wang, H.; Huang, W.; Wang, L.; Zhu, S.; Guan, S. Protective nature of cerium-based oxides coating against Mg corrosion in Hanks' balanced salt solution. *Corros. Sci.* **2023**, *219*, 111255. [\[CrossRef\]](#)
29. Hussain, C.M.; Verma, C.; Aslam, J.; Aslam, R.; Zehra, S. Corrosion protective coatings. In *Corrosion Protection at the Nanoscale*; Elsevier BV: Amsterdam, The Netherlands, 2023; pp. 283–321. [\[CrossRef\]](#)
30. Liu, X.; Chu, P.K.; Ding, C. Surface modification of titanium, titanium alloys, and related materials for biomedical applications. *Mater. Sci. Eng. R Rep.* **2004**, *47*, 49–121. [\[CrossRef\]](#)
31. Mischler, S. Triboelectrochemical techniques and interpretation methods in tribocorrosion: A comparative evaluation. *Tribol. Int.* **2008**, *41*, 573–583. [\[CrossRef\]](#)
32. Bai, H.; Zhong, L.; Kang, L.; Liu, J.; Zhuang, W.; Lv, Z.; Xu, Y. A review on wear-resistant coating with high hardness and high toughness on the surface of titanium alloy. *J. Alloys Compd.* **2021**, *882*, 160645. [\[CrossRef\]](#)
33. Landolt, D.; Mischler, S. *Tribocorrosion of Passive Metals and Coatings*; Elsevier: Amsterdam, The Netherlands, 2011.

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