SiC- and Ag-SiC-Doped Hydroxyapatite Coatings Grown Using Magnetron Sputtering on Ti Alloy for Biomedical Application

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Abstract: SiC- and Ag-SiC-doped hydroxyapatite (HA) coatings were deposited via magnetron sputtering aiming at increased corrosion protection of Ti-10Nb-10Zr-5Ta alloy in simulated body fluid environment and superior mechanical properties compared to plain hydroxyapatite. The coatings had a total thickness of about 350 nm. The X-ray diffraction patterns indicate that HA coatings are polycrystalline with a hexagonal structure and the addition of SiC determined the coating amorphization. All coatings presented a lower roughness compared to the Ti alloy and were hydrophilic. Ag-SiC-HA coating presented the best corrosion resistance and tribological parameters. All coatings were biocompatible, as ascertained via indirect cytocompatibility studies conducted on Vero cells.

Keywords: hydroxyapatite; SiC- and Ag-SiC-doped hydroxyapatite; magnetron sputtering; structure; corrosion and tribological evaluation; in vitro biocompatibility test

1. Introduction

Despite significant improvements in the development of biomaterials aimed at improving their durability, medical implants are not yet perfect. The most frequent fixation problems are related to the need for a stable connection between the implant surface and the surrounding material, and this is one of the most important prerequisites for the long-term success of such fixations. The traditional materials used for implants for hip, knee, shoulder and intervertebral disk replacement (stainless steel 316, Co-Cr alloys, Ti and its alloys, ceramics, polyethylene and polyurethane) have good mechanical properties and high load carrying capacity. Their surfaces are bio-inert but exhibit limited ability to bond and interlock with adjacent bone, such as their reduced resistance to interfacial shearing forces causes implant loosening [1–3].

It is widely accepted that the mechanical property of the implant scaffold has a significant role in controlling the local environment and growth of the adhered cells on it [4,5]. The low mechanical compatibility with bone tissue of the currently used bio-alloys is mainly due to their higher elastic modulus compared to bone, inducing stress shielding and bone resorption, up to implant failure [1–5]. Bone’s Young’s modulus is quite low (7–30 GPa) [1,6] compared to metals (Cp-Ti: 103–107 GPa; Ti-6Al-4V: 114–120 GPa [1,7]), justifying the need for more elastic Ti alloys. Furthermore, their limited biological compatibility with the surrounding bone tissue is due to inadequate corrosion resistance in body
fluids and a high rate of toxic ions release (as Co, Cr, Al, V), which provoke a harmful inflammatory response of the body. Furthermore, the release of inflammatory debris to the surrounding peri-implant tissues and body organs, mainly due to the low tribo-corrosion resistance in biological fluids, occurs in all implants but is more visible in the case of cervical and lumbar discs. The head and acetabular cup are also responsible for the reported implant failure [1–3,8]. Another shortcoming is represented by the low osseointegration of implants, which causes bone atrophy [3,9].

Due to these shortcomings, new Ti alloys with higher bio- and mechanical compatibility and distinctive surface treatments have been developed, in an attempt to avoid different types of implant failure. Therefore, new solutions were investigated, aiming at an increase of corrosion resistance and biocompatibility. Various binary, ternary and quaternary Ti alloys containing elements considered to be safe (Ti, Ta, Nb, Zr and Fe) [1,6,7], such as Ti-15Zr-5Nb [8], Ti-15Ta-15Nb [10], Ti-15Nb-5Zr-4Sn-1Fe [11] and Ti-29Nb-9Ta-10Zr [12–14], demonstrated superior mechanical properties and corrosion resistance compared to commercial alloys and CpTi [1,8,11,15].

To further increase the performance and service life of orthopedic implants, the material’s surface composition, structure and morphology can be modified to improve the bulk properties. The coatings aimed for use on metallic implants are designed to overcome the drawbacks of actual commercial reconstruction implant materials in terms of biological and mechanical compatibility, and tribo-corrosion resistance in physiological fluids (wear in simulated body fluids included), and to maintain or increase the biocompatibility, such as to provide a longer life in patients’ bodies and to improve patients’ life quality. In order to obtain the needed improvement of surface properties for increased osseointegration and consequently extended service life of titanium-based vertebral disks or other artificial joints, various surface treatments which can produce a bioactive layer should be considered. This may secure a robust and durable implant–bone interface, producing the required structural, biochemical and functional stability [9,16]. Hydroxyapatite (HA—Ca₁₀(PO₄)₆(OH)₂) coating is known as one of the popular choices leading to metallic implants osteointegration. Considering HA osseointegration properties, the coating is applied on the stem part of the implants, enhancing the bonding property between metallic implants and bone [17–19], because it offers a consistent milieu for osseointegration, promoting rapid bone formation, and a stable fusion mass with less potential for implant migration, offering the desired implant stability. HA coatings are generally acknowledged as the material of choice because of their capability to connect both structurally and functionally with the human bone [20,21]. Adding reinforcing agent into the hydroxyapatite coating represents a feasible approach to obtain the desired coating–substrate interface [22,23]. The improvement of the HA coatings via addition of different elements has been extensively studied and reported in the literature [24,25]. Lately, numerous cation-doped HA studies have been reported, such as Ag, Zn, Sr and Mg doping, as reviewed by Ratnayake [26]. The such produced amelioration of surface properties allows the preservation of a stable interface between the implant and the host tissue at the cellular level, preventing it from immune reactions, peri-prosthetic osteolysis and also bacterial attacks, if Ag or Zn are used.

The mechanisms of implant failure have recently been the target of intensive research aimed at increasing their service life. Infections start from bacterial colonization of the implant surfaces, leading to the formation of a biofilm matrix that protects bacteria from the host immune system and also from antibiotics, allowing proliferation and, possibly, colonization of other sites. Implant infection treatment requires implant removal and revision surgeries, as the prevention of these infections is of primary importance and must be preferred over their treatment [27]. Considering spine implants, it was reported that infection of both the surgery site and implant might be the origin for constant pain, implant loosening and eventually failed back surgery syndrome. It was reported that chronic infection was observed in about one third of revision cases [28]. Because the specific
infection mechanisms and the potential clinical correlations are uncertain, the best strategy is to use implants with antibacterial properties.

The present work is justified by the results reported in the last 15 years, which demonstrated that the most important causes of implant loosening are due to reduced osseointegration, implant friction, abrasive wear and infection [1,3,26,29]. It is now well documented in spinal surgery that the released spinal implant debris induces inflammation and osteolysis, lessening the implant longevity, and eventually revision surgeries are expected, mainly in younger patients. Considering the increasing number of people needing spine arthroplasty implants, combined with the imminent issue of biologic reactivity, there is a growing need for new implant materials with superior surface properties in terms of tribology, corrosion resistance, bactericide and biocompatibility [29].

In this study, the surface functionalization of the bio-alloy via coatings is addressing the issues related to the development of doped HA coatings for improved osseointegration and reduced infection of the implanted stem. The biological apatite comprises calcium phosphate containing several substitute ions within the apatite lattice, as anionic or cationic substitutes [30]. Subsequently, we report on the deposition via magnetron sputtering of two types of ion-substituted apatite, instead of plain stoichiometric hydroxyapatite, SiC- and Ag-SiC-doped HA coatings, and their characterization in terms of elemental composition, crystallographic structure, corrosion resistance in simulated body fluid (SBF), adhesion to the substrate, wettability and mechanical and tribological properties in SBF environment, compared to the plain HA coating. In addition, in vitro evaluation of cytocompatibility via indirect cytocompatibility studies was carried out.

The following coatings were considered: HA doped with SiC, HA doped with SiC and Ag and plain HA coating as reference. The inorganic additives (SiC and Ag) were selected to be introduced in the HA structure due to the natural occurrence of their component elements in the human body, their biocompatibility and the respective bactericidal effect of Ag. Specifically, SiC was added because the doped HA coatings present enhanced adhesion to the substrate and superior anti-corrosive behavior [31,32]. The choice of using Ag as an antibacterial component was based on the fact that both antibiotic systemic therapy (gold standard) and the controlled local release of organic antibiotics are affected by severe drawbacks such as systemic toxicity, limited efficacy and the development of resistant bacterial strains, such as the inorganic antibacterial coatings appearing extremely appealing [33]. The coatings were deposited on Ti-10Nb-10Zr-5Ta (TNZT) alloy, because it exhibits superior tensile properties, its Young’s modulus during deformation is close to the cortical bone and its corrosion resistance is superior to Ti6Al4V alloy in simulated body fluid (SBF) [13].

2. Materials and Methods

2.1. Coating and Specimens

The HA and doped HA coatings were produced via a RF magnetron sputtering method using a magnetron deposition system equipped with 5 cathodes (2.54 cm diameter), arranged in a confocal configuration—ATC ORION (AJA International Inc., Scituate, MA, USA). The base pressure in the system was $8 \times 10^{-4}$ Pa, and a deposition pressure of 0.67 Pa was maintained via Ar flow, introduced using a mass flow controller. For the deposition we used the following targets: Ag (99.99% purity) and SiC (99.5% purity) from Kurt J. Lesker Company (Hastings, UK) and HA targets (99.5% purity) from Testbourne Ltd. (Basingstoke, UK).

The substrates were (111) Si square coupons (l = 10 mm), cut from wafers (Si-Mat Silicon Materials e.k., Kaufering, Germany) and discs of Ti-10Nb-10Zr-5Ta alloy, from R&D Consultanta si Servicii SRL (Bucharest, Romania), 2 mm thick and 20 and 18 mm in diameter.

The Ti–10Nb–10Zr–5Ta alloy discs were polished with progressively finer emery papers (up to 2.5 μm median diameter corresponding to European P4000—FEPA Standard
43-2:2017—or J4000—Japanese Industrial Standard JIS R 6001:2017 grit) and then with 0.5 μm diamond suspension. The sample surface roughness was determined with a surface profilometer (Dektak 150, Bruker, Billerica, MA, USA), scanning ten random chosen areas of (1 × 1) mm². The data were averaged and statistically analyzed via a paired Student’s t-test (p ≤ 0.01). The polishing protocol with diamond suspension was repeated until a roughness value of (90 ± 6) nm was attained. The cleaning of all substrates was done in an ultrasonic bath using acetone, then in isopropyl alcohol and finally in distilled water, and they were then flushed with dried nitrogen.

The clean substrates were introduced in the deposition chamber, located at 170 mm from the sputtering targets on a rotating holder, outfitted with a backside non-contact thermocouple for substrate temperature measurement. Before starting the deposition process, the substrates were heated until reaching the deposition temperature (700 °C). Afterwards, the removal of any remnant contaminant layer on uncoated sample surfaces was done via sputtering in Ar, applying −320 V on the substrates, at 0.67 Pa for 15 min.

Magnetron sputter techniques are a versatile method, enabling the deposition of various materials, if the deposition conditions are carefully chosen. To get a quite stoichiometric HA composition, provisions are to be made for the deposition parameters, which should be chosen with caution. The RF power on HA coatings was so selected to permit a suitable deposition rate (considering the deposition time for a certain thickness) but taking care not to permit the development of small arcs which provoke the discharge interruption [34]. The RF power on the SiC target was chosen such that the Si concentration was about 7 at.%, considering that different concentrations of Si in magnetron-sputtered Si-doped HA were previously reported (1.8 wt.%, 4.2 wt.% and 13.4 wt.%), indicating coating amorphization and decreased surface roughness [35]. Infection prevention at the implant location is one major concern. Probably the oldest and still the actual way to prevent such infections is based on the use of Ag. The reported results indicate that Ag in equally atomic and ionic states has low toxicity to human cells [36]. In addition, Ag incorporation in different biomaterials, HA included [37], indicates that bacteria show a low propensity for acquiring resistance to Ag-containing materials, even in minute concentrations [38]. However, reports show that high Ag concentrations are cytotoxic, the maximum toxic concentration for human cells being 10 mg/L of Ag [39]. Considering the above, Ag current fed on Ag magnetron was chosen to get a concentration of about 1 at. %.

The coatings were deposited as follows: HA coatings—2 × HA targets; SiC-HA coatings—2 × HA targets and 1 × SiC; Ag-SiC-HA coating—2 × HA targets, 1 × SiC and 1 × Ag. The HA and SiC targets were fed by RF power, while the silver target was fed by direct current (DC) power (constant current mode). Aiming to obtain crystalline coatings, the substrate RF bias was set at −30 V, and the deposition temperature was maintained at (700 ± 4) °C, as previously reported [40]. As known, a high temperature during deposition or during coating annealing improves the coating crystallinity and surface morphology [41,42]. The RF power or the DC current fed on each magnetron are presented in Table 1 along with the labels assigned to the HA-based coatings. Due to the different sputtering rate of each type of target, the deposition duration varied from 260 to 235 min, in order to produce films of about 350 nm thickness.

| Table 1. Deposition parameters of the HA-based coatings. |
|------------------|--------------|--------------|----------------|----------------|----------------|
| Coating          | P(HA) [W]    | P(SiC) [W]   | I(Ag) [mA]     | Ubias [V]      | Deposition (min) |
| HA               | 2 × 120      |              | -              | −30            | 260            |
| SiC-HA           | 2 × 120      | 1 × 15       | -              | −30            | 240            |
| Ag-SiC-HA        | 2 × 120      | 1 × 15       | 2              | −30            | 235            |

For all characterization tests, in order to get the necessary number of replicates, each type of coating was deposited on a Si coupon and TNZT discs with different diameter
values: 8 pieces of $\phi = 20$ mm and 12 pieces of $\phi = 18$ mm, the last ones for the in vitro tests.

2.2. Coatings Characterization

2.2.1. Elemental and Phase Composition

A Quantax 70 (Bruker, Billerica, MA, USA) system equipped with a XFlash 430 H detector (detection limit of 0.1 wt.% [43]), integrated in a TM3000 Tabletop SEM (Hitachi, Tokyo, Japan), was used to determine the elemental composition of the coatings via energy-dispersive X-ray spectroscopy (EDS). We did not use any standard samples, as we calculated the precision in EDS measurements using the relative standard deviation (RSD) expressed as the product of standard deviation (SD(%)) and the arithmetic mean content of each constituent element: $\text{RDS(\%)} = 100 \times (\text{SD(\%)} \times \text{mean \% content})$, where SD represents the standard deviation of element “i” calculated after 10 measurements, 5 on each of the two replicates of each type of coating in different areas, and C represents the arithmetic mean content of the constituent element “i”. In order to improve the measurement accuracy, we used long counting (acquisition) times, which are reported to generate RSD of about 1% [44,45].

The crystallographic structure of the films was investigated using an X-ray diffraction technique with a SmartLab diffractometer (Rigaku, Tokyo, Japan), equipped with a 9 kW Cu rotating anti-cathode, a vertical goniometer of 300 mm radius with sample horizontal mount and a HyPix 3000 two-dimensional semiconductor detector. The diffractometer was operated in parallel beam alignment geometry. The X-ray optics of the incident beam included a parabolic multilayer mirror to form the parallel beam, a 2-bounces Ge(220) monochromator to select out only Cu Kα1 radiation ($\lambda = 1.540597 \, \text{Å}$) and vertical and horizontal limiting slits of 1 mm and 5 mm width, respectively. The horizontal divergence of the diffracted beam was limited to $5^\circ$ by Soller slits located between two vertical slits of 1 mm and 1.1 mm width, respectively, and 20/0 diffractograms were recorded over a 20°–60° range with a resolution of 0.025°. The diffractograms were analyzed using Rigaku’s PDXL software package (version 2).

The Fourier transform infrared (FT-IR) spectra of the films deposited on Si (100) substrates were obtained using a Jasco 6300 spectrometer (Jasco Corporation, Hachioji, Japan). All IR spectra were assessed in the transmission mode and averaged over 150 scans, in the spectral region of 4000–400 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. A bare Si(100) substrate was used as reference to eliminate any substrate signal contribution to IR spectra of the samples.

2.2.2. Surface Roughness, Morphology and Wettability

The surface roughness was measured using a Dektak 150 surface profilometer (Bruker, Billerica, MA, USA). The roughness measurements were carried out on two replicates in 5 randomly chosen different areas, and the results were averaged. The coatings’ roughness was determined over a length of 10 mm for 200 s and the $R_a$ (arithmetic average) roughness parameter was determined.

The surface morphology of the TNZT alloy and the coated samples was examined using a scanning electron microscope (SEM, TableTop 3030 PLUS).

The wettability of the coatings with SBF solution (SBF composition: 8.035 g/L NaCl, 0.335 g/L NaHCO$_3$, 0.225 g/L KCl, 0.231 g/L KHPO$_4$·3H$_2$O, 0.311 g/L MgCl$_2$·6H$_2$O, 0.292 g/L CaCl$_2$, 0.072 g/L Na$_2$SO$_4$, 6.228 g/L (HOCH$_2$)$_3$CNH$_2$) with pH = 7.4 was assessed via contact angle measurements, carried out using KSV-Devices Attention TL101 equipment (Biolin Scientific, Stockholm, Sweden), at room temperature ($25 \pm 1 \, ^\circ\mathrm{C}$), using a micro-syringe (Hamilton Company, Reno, NV, USA) to weep the solution. Each experiment was run on two replicates. Five SBF droplets were poured on different regions of the samples, in order to improve statistics and to reduce the measurement errors. The contact angle was measured at each run and the averaged value was considered. Prior to the
measurements, the surfaces of each sample were cleaned using a CO2 snow cleaner (Applied Surface Technologies, Providence, NJ, USA).

2.2.3. Electrochemical Analysis

The corrosion tests were conducted in SBF solution (pH = 7.4) at 37 ±1 °C. The SBF solution was selected because it is one of most used artificial solutions with a composition appropriate for human body fluids, being prepared according to the values proposed by Kokubo et al. [46]. The tests were carried out using a VersaSTAT 3 Potentiostat (Princeton Applied Research). The electrochemical cell was equipped with the typical three electrodes: one made of Pt (reference electrode), the second made of saturated calomel (counter electrode, SCE) and the third (reference electrode) was the investigated sample. Each sample was inserted in a special holder made of Teflon in order to keep a known area in direct contact with corrosive solution (1 cm²). The open-circuit potential (Eoc) was monitored for 1 h after immediate samples’ immersion. The Tafel curves were recorded at ±250 mV vs. The Eoc was at a scanning rate of 0.167 mV/s. The potentiodynamic polarization curves ranged from −1 V vs. Eoc to +1.5 V vs. SCE, at a scanning rate of 0.167 mV/s. Experiments were performed according to ASTM G 59-97 (2014) standard. For repeatability, the tests were carried out on two different samples prepared with the same conditions. Via graphical extrapolation of the cathodic and anodic branches of the polarization curves in the range of ±50 mV, the corrosion potential (Ecorr = 0) and the corrosion current density (icorr) were determined.

2.2.4. Mechanical Properties

The hardness (H) and reduced Young’s modulus (Er) were determined via nanoindentation tests using a computer-controlled Nanoindenter (TI Premier Hysitron (Bruker, Billerica, MA, USA)) equipped with a Berkovich-type diamond tip. The measurements were carried out using a continuous stiffness measurement method. The data from four test points were acquired for each maximum penetration depth, to validate the tests consistency. As the interactions among the test points may result in erroneous data, mainly for soft coatings, the spacing between each of them was set to a minimum of 150 μm.

The coatings’ adhesion to the substrate represents an essential attribute of a coating for its appropriate functioning. The evaluation of the coating adhesion strength to TNZT substrate was carried out using Bruker’s Universal test system (UMT TriboLab™ (Bruker, Billerica, MA, USA)). We used a typical progressive linear load scratch test (according to the EN1071-3:2005 standard specified conditions), in which the stylus is moved over the coating’s surface with a linearly increasing load until a failure occurs. We used a Rockwell stylus (angle—119°59’, radius—195 μm). The maximum applied force was 50 N, and the scratching distance and duration was 10 mm and 60 s, respectively. The test completed, the coating’s scratch failure mode was inspected using an in-built optical microscope, revealing the normal load at which such failure occurs, known as the critical load (Lc).

2.2.5. Tribological Properties

The tribological performance in SBF solution of the uncoated and coated samples was studied at 37 ±1 °C using a ball-on-disc tribometer (CSM Instruments SA | A company of Anton Paar, Peseux, Switzerland). The bare and coated TNZT discs were used as a plate, and the counterpart for the sliding tests was a sapphire ball with a diameter of 6 mm, pressed against the coating with a normal load (F) of 0.72 N, on a distance (d) of 300 μm and with a sliding speed (v) of 10 cm/s.

The tribological measurements were repeated three times, using three replicates, in order to get reliable results.

The wear rate K was calculated to quantify the wear resistance as: K = V/(F×d), where V is the worn volume. The worn volume V was determined using a Dektak 150 surface
profilometer by measuring six lines on each track and deriving the cross sectional area of the wear track. The measurements were done on each wear track of the three replicates, and the averaged value was considered.

2.2.6. In Vitro Evaluation of Cytocompatibility by Indirect Cytocompatibility Studies

The evaluation was carried out via indirect cytocompatibility studies. The test materials were incubated in Eagle’s minimum essential medium (MEM) for 24 h at 37 °C according to ISO 10993-5 [47] standards (surface area to volume ratio of the specimen to cell culture medium was 3 cm²/mL) and the medium containing the extract was collected. Vero cells (American Type Culture Collection), a lineage that is recommended to be used in studies of cytotoxicity for biomaterial validation, were seeded at a density of 7500 cells/cm² in 96-well tissue culture plates and maintained in MEM culture medium supplemented with 10% fetal bovine serum (FBS) and 1% penicillin/streptomycin in a humidified atmosphere of 5% CO₂ at 37 °C for 24 h. After this time, the culture medium was removed and replaced with the extraction medium for additional culture for 24 h. Further, cell viability and metabolic activity were measured using CCK8 assay. Briefly, cells were rinsed with PBS and a solution containing 10 μL of CCK-8 solution (Sigma-Aldrich Co., St. Louis, MO, USA), and 100 μL of culture medium was added in each well. They were then incubated for 3 h at 37 °C. Then, the absorbances of the incubated solutions were measured at 450 nm and recorded using a microplate reader (Thermo Scientific Appliskan, Vantaa, Finland). The intensity of the color obtained is directly proportional to the metabolic activity of the cell populations and inversely proportional to the toxicity of the material and, consequently, its extract. A solution of MEM + 5% of dimethylsulfoxid (DMSO), which is considered cytotoxic, served as a cytotoxicity positive control and the standard culture medium was used as a negative control. After the incubation of cells with sample extracts, cell cultures were examined via phase-contrast microscopy. The morphology of the cells was assessed in comparison to negative and positive controls.

3. Results and Discussions

3.1. Surface Morphology, Elemental and Phase Composition of the Investigated Samples

Table 2 presents the elemental composition of the TNZT alloy used in this study, determined via EDS, and the relative standard deviation (RDS). The alloy presented a homogeneous composition, as evidenced via EDS analysis and presented in Figure 1. The results are in good agreement with the previously reported composition [13].

| Element | Ti    | Nb    | Zr    | Ta    |
|---------|-------|-------|-------|-------|
| Composition (wt.%) | 74.9 ± 3.1 | 9.7 ± 1.6 | 9.9 ± 1.4 | 5.4 ± 0.6 |

Figure 1. Homogeneous element distribution of the TNZT alloy (magnification 100×).

Table 3 presents the mean values of the atomic concentrations of the constituent elements, measured for each type of coating, together with Ca/P concentration ratios. HA coatings have the Ca/P ratios close to the value specific for the stoichiometric
hydroxyapatite. Si addition in HA determines the decrease of this ratio, as Si replaces P in the PO$_3^-$ site [48]. The addition of Ag as cationic replacement of Ca [49] determines a slight increase of the ratio. The elements distribution on the coated TNZT alloy is presented in Figure 2. In order to have a better image of the coatings’ homogeneity, each element in the element distribution diagram is stripped out and presented in Figure 2d for the Ag-SiC-HA coating. As expected, the elements of the substrate are also visible.

Table 3. The elemental composition of the Ti–10Nb–10Zr–5Ta alloy.

| Coating     | Elemental Composition (at. %) | (Ca + Ag)/(P + Si) |
|-------------|-------------------------------|------------------|
|             | Ca   | P   | O   | Si  | C   | Ag  | Si  |
| HA          | 21.11 ± 0.68 | 12.54 ± 0.43 | 66.34 ± 4.60 | -   | -   | -   | 1.68 |
| SiC-HA      | 19.79 ± 0.61 | 4.45 ± 0.13  | 60.60 ± 4.53 | 7.37 ± 0.25 | 7.80 ± 0.24 | -   | 1.67 |
| Ag-SiC-HA   | 20.54 ± 0.75 | 5.22 ± 0.15  | 58.43 ± 4.20 | 7.57 ± 0.22 | 7.06 ± 0.23 | 1.08 ± 0.12 | 1.69 |

Figure 2. Coated TNZT alloy: element distribution on HA (a), SiC-HA (b) and Ag-SiC-HA (c) coatings (magnification 100×); (d) distribution of each individual element in Ag-SiC-HA coating.

The crystallographic structure of all the deposited coatings was determined on one replicate of each type of coating deposited on TNZT alloy and Si. The X-ray diffraction patterns of the coatings deposited on the TNZT alloy are presented in Figure 3, along with the XRD pattern of the bare alloy. TNZT alloy presents the hexagonal α’ martensite structure (cell parameters: a = 0.2993 nm, c = 0.4642 nm), and the β bcc phase (a small peak partially overlapped on α’ maximum). A grain size value of 20.9 ± 0.3 nm was obtained
for $\alpha'$ phase, derived from the (101) maximum peak using the Scherrer formula [50]. The TNZT structure is similar to the ones reported for other TiNbZrTa alloys, with different elements concentrations [51,52].

![Diffraction patterns of the bare and coated Ti–10Nb–10Zr–5Ta alloy.](image)

**Figure 3.** Diffraction patterns of the bare and coated Ti–10Nb–10Zr–5Ta alloy.

The following JCPDS cards were used to identify the lines of the coatings and substrate: 055–0592 for HA (hexagonal structure, space group P63/m(176)), 04–0783 for Ag (face centered cubic close-packed structure, space group Fm-3m(225)) and 05–0565 for Si (face centered diamond cubic structure, space group Fd-3m(227)). All four peaks of the TNZT substrate are situated in the proximity of either HA or Ag peaks, as follows: $\alpha'(100) = 34.62^\circ$ is situated in between HA(300) $= 32.91^\circ$ and HA(301) $= 35.481^\circ$, $\alpha'(002)$ and $\beta(110) = 38.00^\circ$ are situated near Ag(111) $= 38.18^\circ$, $\alpha'(101) = 39.62^\circ$ is situated near HA(310) $= 39.82^\circ$, and $\alpha'(102) = 52.56^\circ$ is located in close proximity to HA(004) $= 53.19^\circ$. The diffraction patterns of doped HA coatings evidenced the specific HA hexagonal structure, while other phases related to the formation of silicon oxides or sub-species of calcium phosphate were not substantiated.

The undoped HA coating presented a polycrystalline hexagonal structure (space group: P63/m(176)), with an intense (002) maximum, while SiC-HA and Ag-SiC-HA exhibited only a few orientations: HA(301), HA(310) and HA(004). It is to note that the (004) maximum of HA can be differentiated quite well from the $\alpha'(102)$ maximum of TNZT. Furthermore, the SiC and Ag addition shift the maximum position to lower angles, towards $\alpha'(102)$ peak position, indicative for a cell expansion due to doping elements. The above patterns indicate that all coatings seem to grow with a texture similar to the one of the TNZT substrate. It is evident that the diffractograms of SiC-HA and Ag-SiC-HA coatings present only maxima superposed in close vicinity to the substrate peaks, indicating coatings amorphization, as also reported for magnetron deposited coatings [35]. To avoid this superposition, we investigated also the coatings deposited on Si substrates, their patterns being presented in Figure 4. It is to note that the positions of the HA(300) plane ($2\theta = 32.91^\circ$) and of the Si(002) plane ($2\theta = 32.96^\circ$) are superimposed.
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Figure 4. Diffraction patterns of the HA and doped HA coatings deposited on Si substrates.

Considering the diffractograms of the HA coatings deposited on alloy and silicon, one can observe a higher number of maxima compared to the coatings deposited on TNZT alloy. The most intense maxima of the coatings deposited on Si are also those corresponding to (002) and (004) planes. Contributions from (102), (112), (202), (212), (400), (203), (222), (213) and (104) peaks are also visible on the HA diffractogram. Compared to the reference data, the calculated cell parameters of the HA coatings indicated a larger value of the “a” parameter (9.429(6) Å vs. 9.4180 Å) and lower value for the “c” parameter (6.867(3) Å vs. 6.8840 Å), with a cell volume almost identical to the reference value: 528.8(5) Å³ vs. 528.797 Å³. The crystallite size and the strain, calculated using the Williamson–Hall method, were 29.2(29) nm and 0.08(13)% respectively, indicating a slight deformation of the HA cell. The presence of strain is common for coatings deposited via magnetron sputtering, mainly if the deposition is carried out at high temperature and assisted by ion bombardment generated by the applied substrate bias.

The addition of SiC to HA determined a clear amorphization of the coating, derived from the disappearing of the most important maxima: (002), (102), (211), (112), (202), (212), (213) and (104). The peak corresponding to the HA(300) plane overlaps the Si(002) peak; therefore, it is uncertain if it can be ascribed also to hexagonal HA, as we considered only the HA(400) plane. Due to the presence of only one certain maximum, it was possible to calculate only the value of the “a”, indicating an increase of about 8% due to SiC addition. The amorphization of HA at Si or SiC addition is well documented in the literature, despite the synthesis method [31,48,53].

The Ag addition to the SiC-HA coating showed the appearance of the (111) and (202) maxima of the cubic Ag, with no other change from the almost amorphous SiC-HA structure. The “a” cell parameter of the cubic Ag, derived from the Ag(111) maximum was 4.0878 Å, higher than the reference one, of 4.0862 Å. The presence of an Ag(200) peak enlarged the observed peak at 44.25°, which included Ag(200) and HA(400) maxima. The “a” cell parameter calculated for the HA hexagonal structure after maximum decomposition in two peaks was 9.4497 Å, indicating a further increase of about 14% vs. SiC-HA.

The assumed hexagonal structure of the HA coatings is based on the literature data [54–56]. As discussed by Morgan et al. [54], if HA is to some extent non-stoichiometric or even slightly doped, it presents a hexagonal structure (space group P63/m). However, the compound strictly stoichiometric is monoclinic (space group P21/b) [55,56], but this structure can be synthesized only at high preparation temperatures (>900 °C) [56]. Consequently, even if the monoclinic structure (JCDPS card 01-089-4405) has in common with the hexagonal structure the main peaks visible on the diffractograms of the deposited HA based coatings, the coatings deposition took place at a lower temperature than the one
necessary for obtaining the monoclinic structure. As reported, all synthesis methods implying lower temperatures produce hexagonal HA structures, probably due to a lack of OH ions, which are substituted by impurity ions or H₂O, as the monoclinic layout is disrupted [54,56].

The phase composition of the coatings was investigated using FT-IR absorption. Figure 5 present the obtained results, which are in good agreement with the XRD analysis, confirming that the HA phase was influenced by SiC addition.

![FTIR spectra of HAP-based coatings.](image)

The spectrum of the HA coatings revealed specific bands situated between 800 and 1200 cm⁻¹, which can be mainly attributed to phosphate functional groups.

For the pure HA coating, strong absorption bands corresponding to HA—ν4 (600 and 571 cm⁻¹), HA—ν1 (962 cm⁻¹) and HA- ν3 (1086, 1053 and 1032 cm⁻¹) were identified [57]. As it can be noticed in Figure 5, the IR bands attributed to pure HA coating became wider and shift towards lower wavenumbers after SiC or SiC and Ag were added into the HA structure. Note that no specific absorption bands located between 770 and 680 cm⁻¹ [58,59], corresponding to the SiC stretching bond, were revealed via FT-IR analysis. Previous IR studies have shown that the structure of HA remains unaffected after Ag addition [60,61], whereas SiC addition leads to crystallinity decrease in HA coatings [53], confirmed by our XRD results. Moreover, the shift and broadening of the aforementioned HA bands can be determined by the overlapping of SiO₂⁺ and PO₄²⁻ vibration modes in the 1100–900 cm⁻¹ region [58,62,63]. The presence of OH group bands observed between 4000 and 3500 cm⁻¹ in all samples can be associated with the absorbed H₂O molecules on the sample’s surface.

3.2. Surface Morphology and Wettability

Figure 6a–d shows the SEM micrographs of the bare and coated TNZT substrates. The coated substrates exhibited much smoother surfaces than the alloy substrate. One can observe that the morphology of all coated surfaces is similar, and the small differences are expressed by the specific roughness parameter R. The decrease of the roughness at SiC addition is probably related to the coating amorphization, as evidenced via XRD. Considering the associated errors, silver addition to SiC-HA coatings resulted in a small decrease of the roughness compared to the HA coating, specific for the metal addition to HA coatings [35,64,65].
It is well known that the wettability of biomaterials is a factor which significantly influences their biocompatibility, as the protein absorption is promoted by superior wettability [66,67]. Figure 7 presents the images of the SBF droplets on the surfaces of the uncoated and coated TNZT substrate, the measured values of the contact angle and the averaged surface roughness Ra.

![Figure 6](image_url)  
**Figure 6.** SEM micrographs (×500, 200 μm) of the bare and coated TNZT alloy: TNZT (a), HA/TNZT (b), SiC-HA/TNZT (c), Ag-SiC-HA/TNZT (d).

![Figure 7](image_url)  
**Figure 7.** Images of the SBF droplets on the surfaces, the measured values of the contact angle (CA) and average roughness parameter (Ra) for the TNZT alloy (a) and three types of coatings: HA (b), SiC-HA (c) and Ag-SiC-HA (d).

As generally acknowledged, a solid surface is considered hydrophobic if the water contact angle (CA) is higher than 90°, as the limit between hydrophilicity and hydrophobicity is set at 90°. However, when using different water-based solutions, the above value may vary. Previous experiments indicated that on the currently used TiAlV alloy the CA of SBF is higher (78.25° ± 1.62°) than the CA of water (74.75° ± 1.62°). Consequently, even if the hydrophilicity limit was maintained at 90°, all deposited coatings proved to be hydrophilic when SBF solution was used.

As observed, the addition of SiC increases the hydrophobicity of the coating, while the supplementary addition of Ag determines its decrease. Considering the measurement errors for the CA and Ra, it was evidenced that SiC addition determined a shift towards hydrophobicity, while the Ag addition restored the equilibrium towards hydrophilicity. However, it is remarkable that all HA-based coatings retained the hydrophilic character.

### 3.3. Corrosion Resistance

The evolution of Eoc in time is presented in Figure 8. The open-circuit potential (Eoc) varies over time until attaining a stable value. The time period is dependent on the material’s ability to form a more stable oxidized state in the corrosive environment.
Figure 8. The time evolution of the open circuit potential (Eoc) for uncoated and coated TNZT alloy.

The TNZT alloy was quickly oxidized, as the transitional metals from the periodic groups IVB and VB are known to be prone to oxidation. It should be noted that TNZT alloy is stable in various corrosive solutions over more than 24 h such as Fusayama artificial saliva solution doped with NaF and different pH values [68], Fusayama-Mayer artificial saliva or SBF [13].

All HA-based coatings attained a stable value easily due to their ceramic character. The highest Eoc value was observed after Ag was added to the SiC-HA coating, presumably due to Ag nobility. For the SiC-doped HA a Eoc decrease was evidenced at the beginning of the immersion period; however, its evolution become stable after ~2400 s, reaching the same value as the HA coating of ~0.22 mV. The Eoc value obtained for HA and SiC-HA coatings was the lowest. On the contrary, the Ag-SiC-HA coating exhibited the highest value (~0.07 mV).

After 40 min of immersion all coatings exhibited a stable Eoc value, indicating the formation of passive films on their surfaces. At the end of the test, the Eoc values measured for all investigated surfaces are more similar (differences are under 0.1 V), indicating a similar behavior after 1 h of immersion.

Figure 9 presents the potentiodynamic polarization curves of the uncoated and coated samples in SBF solution. Based on the polarization curves, the electrochemical parameters were extracted by fitting the Butler-Volmer equation, which described the changes in a sample’s potential when subject to an external potential:

\[ I = I_{corr} \left[ \exp \left( -\frac{\alpha_e F \eta}{RT} \right) - \exp \left( -\frac{\alpha_a F \eta}{RT} \right) \right] \]  \hspace{1cm} (1)

where: \( I \)—the external current density, \( R \)—the ideal gas constant, \( F \)—the Faraday constant, \( T \)—the absolute temperature, \( I_{corr} \)—the corrosion current density, \( \eta \)—the over potential \( (\eta = V_{applied} - E_{OCP}) \) its exact value is determined via unitless transfer coefficients for the cathodic and anodic currents \( (\alpha_e \ and \ \alpha_a) \). At \( E_{OCP} \ \eta = 0 \), the anodic and cathodic currents are equal and the external current I is zero, as no current flows to or from the sample electrode. The above form of the Butler-Volmer equation is compatible with multi-electron processes. Concurring with up-to-date references [69,70], the values of the transfer coefficient should not be scaled by the number of electrons transferred.
Figure 9. The potentiodynamic plots of the uncoated and coated samples in SBF corrosive solution at 37 ± 0.4 °C.

Table 4 presents the values of the electrochemical parameters obtained at the end of the tests. From the Tafel curves, via graphical extrapolation of the cathodic and anodic branches of the polarization curves in the range of ± 50 mV, we determined the corrosion potential (E∞) as the zero current electrochemical state of the interface [71]. The measured difference between the anodic and cathodic current, indicative for the corrosion intensity at Tafel’s scanning corrosion potential, represents the corrosion current density, one of the most significant parameters for corrosion resistance assessment.

Table 4. The corrosion parameters of the coatings: open circuit potential (Eoc), corrosion potential (E∞), corrosion current density (icorr), polarization resistance (Rp), porosity (P) and protective efficiency (Pe).

| Sample    | Eoc (mV) | E∞ (mV) | icorr (µA/cm²) | Rp (kΩ) | P          | Pe (%) |
|-----------|----------|---------|----------------|---------|------------|--------|
| TNZT      | –122     | –317    | 226.309        | 1.506   | -          | -      |
| HA        | –234     | –156    | 5.834          | 28.464  | 0.049      | 97.4   |
| SiC-HA    | –216     | –222    | 4.884          | 31.323  | 0.046      | 97.8   |
| Ag-SiC-HA | –73      | –340    | 0.4365         | 177.558 | 0.008      | 99.8   |

The polarization resistance (Rp) was calculated using the Stern-Geary equation [72]:

\[
R_p = \frac{1}{i_{corr}} \left( \frac{\beta_a \beta_c}{\beta_a + \beta_c} \right)
\]  

(2)

The coating porosity (P) was estimated using Elsener’s empirical equation [73]:

\[
P = \left( \frac{R_p_{substrate}}{R_p_{coating}} \right) 10^{-|\Delta E(\text{i}=0)|/\beta_a}
\]

(3)

This parameter corresponds the ratio of all the pores areas to the total exposed surface [74]. If there are fewer pores or defects, the electrolyte access to the substrate is hindered, and the porosity is characterized by low values, indicating a superior corrosion performance [75].

The protective efficiency (Pe) was calculated according to the equation presented in Ref. [76]. It represents the protection conferred by the coating to the bare substrate, whereby higher values indicate higher corrosion protection.

\[
P_e = 1 - \frac{i_{corr,coating}}{i_{corr,substrate}}
\]

(4)

Because the surface roughness has a significant influence on its ability to outstand the corrosion attack, the Ra roughness parameter values measured before and after the corrosion tests are presented in Figure 10.
The highest $E_{\text{oc}}$ value was observed for the Ag-SiC-HA coating, ascribed to the nobility of the silver. It should be noted that the alloy also has a high value of this corrosion parameter, due to the metal’s known ability to quickly oxidize in the presence of water solutions. On the contrary, the HA and SiC-HA coatings presented lower $E_{\text{oc}}$ values. The corrosion potential ($E_{\text{corr}}$) values indicated the lowest values for Ag-SiC-HA and TNZT and the highest for HA and SiC-HA coatings. However, the most significant parameter ascertaining the corrosion resistance is the ion corrosion density ($i_{\text{corr}}$). The lowest $i_{\text{corr}}$ values were found for the Ag-SiC-HA coating, followed by the SiC-HA and HA coatings, and then the uncoated alloy. All coated samples exhibited higher polarization resistance ($R_p$) values compared to the uncoated alloy. A small difference was found between HA and SiC-HA coatings, but the highest $R_p$ value was exhibited by the Ag-SiC-HA coating. In addition, the porosity ($P$) and the protection efficiency ($P_e$) values of the coatings maintained the same rank as the corrosion current density. It should be noted that the Ag-SiC-HA coating exhibited the lowest porosity (0.008). Once more, small differences in porosity were found between HA and SiC-HA coatings. The porosity values are well correlated to the values of polarization resistance $R_p$, which have higher values for the lowest porosity. The protective efficiency ($P_e$) increased with the addition of dopants. The highest value was exhibited by the Ag-SiC-HA coating (99.8%).

These results may be ascribed to the amorphized structure of the doped coatings, such as after the corrosive attack they their roughness remained almost unchanged, indicating that the ingress of the corrosive solution was hindered by their low porosity, ensuing from their amorphized structure, evidenced via XRD.

To exemplify the above findings, Figure 11 presents SEM images of the surface morphology and the corresponding EDS mapping spectra of the bare and coated TNZT alloy, subsequent to the electrochemical tests in SBF at $37 \pm 0.4$ °C. TNZT alloy (Figure 11a) presents a quite corroded surface, with a high degree of oxidation (Figure 11e), as expected. On the surface of the HA coating (Figure 11b), we can see some dark zones, which in EDS mapping (Figure 11f) are associated to a thinner coating and the presence of oxidized metals beneath. The SiC-HA surface also shows corroded bright zones, similar to those evidenced on the bare alloy, indicating that these coatings were affected by SBF solution (Figure 11c). EDS mapping (Figure 11g) shows large zones with unaffected coating and also bluish regions with corroded and thinner coating, but the presence of yet unoxidized alloy is clearly visible. The above images sustain the superior corrosion resistance of the SiC-HA coating compared to the undoped HA.
Figure 11. SEM and EDS images of: TNZT alloy (a,e), HA (b,f), SiC-HA (c,g) and Ag-SiC-HA (d,h) coatings.

The Ag-SiC-HA coating is much more unaffected by the SBF solution; for instance, one can observe large unaffected areas via the electrochemical tests (Figure 11d). This result indicates that this coating has superior corrosion resistance compared with the other two. The EDS analysis of the Ag-SiC-HA surface (Figure 11h) shows a homogenous distribution of both coating and alloy elements, implying the presence of the coating, with a low dissolution grade.

The coating most affected by the corrosion test is presented in Figure 12, and each element in the element distribution diagram is stripped out. One may observe that the Ca and P elements are not present in the corroded region, while in the same region the elements of the substrate are clearly visible. The distribution of oxygen does not follow the one of Ca and P, because during the corrosive attack the metallic elements of the substrate were also oxidized.

Figure 12. EDS images of each element present in HA coatings deposited on TNZT alloy after the corrosion test.

Summarizing the electrochemical, SEM and EDS results we conclude that the SiC and Ag addition into the HA matrix improved the resistance to corrosive attack of SBF solution.

3.4. Mechanical Properties

The HA deposited coatings are aimed at similar properties to natural bone, mainly its osteointegration ability, so the mechanical characteristics (reduced elastic modulus and
hardness) are needed to predict the HA performance when used in specific applications. As known, the values of certain relations between H and E¢ may give important information about the ability of the coatings to adhere to the substrate, so as to achieve a stable interface between the coating and the metallic implant, to prevent the release of any wear debris producing unwanted pain, immune reactions and peri-prosthetic osteolysis. As previously reported, in spine surgery the reactivity of the biological environment to the debris generated by an implant is of major importance because it determines the implant clinical performance in the long term [29].

Due to the expected low hardness of the HA-based coatings and their small thickness, the load-unload measurements were conducted from 0.2 to 0.5 mN, with a 0.1 mN step size. The measurements were carried out at 0.3 mN, in order to have a penetration depth of less than 10% of the film’s thickness. Table 5 presents the averaged values of reduced elastic modulus E¢ and hardness H obtained from load–unload measurements, along with various ratios of H and E¢ values (H/E¢, H/E¢² and H/2E¢).

Table 5. The obtained averaged values of reduced elastic modulus E¢ and hardness H, along with various ratios of H and E¢ values (H/E¢, H/E¢², H/2E¢).

| Sample  | H (GPa) | E¢ (GPa) | H/E¢ | H/E¢² (GPa) | H/2E¢ (GPa) |
|---------|---------|----------|------|-------------|-------------|
| HA      | 7.351 ± 0.201 | 98.245 | 0.075 | 0.041 | 0.275 |
| SiC-HA  | 12.394 ± 0.381 | 126.131 | 0.098 | 0.120 | 0.609 |
| Ag-SiC-HA | 10.628 ± 0.213 | 119.545 | 0.089 | 0.084 | 0.472 |

The SiC addition to HA determines the increase of both hardness and reduced elastic modulus. The H and E¢ values measured for the Ag-SiC-HA coatings indicate a slight decrease of both values, ascribed to the softness of silver.

The plasticity index (H/E¢) defines the elastic strain of a material to its failure. It indicates that both doped HA coatings presented superior values compared to plain HA, pointing to better elastic properties and adhesion to the substrate. The relative resistance of materials to plastic deformation might be gauged by comparing their specific H/E¢² ratios [77]. The superior resistance of the doped HA coatings compared to the plain HA coating is obvious. Again, the best results were exhibited by SiC-HA, but Ag-SiC-HA exhibited however a value significantly higher (>2) than the plain HA. The H/2E¢ ratio, also known as the modulus of resilience, expresses a material’s resistance to the effect of external forces. Again, the SiC-HA coating presented the highest value for the modulus of resilience. However, the measured value indicated that both doped HA coatings exhibited good ability to recover when subject to external forces. The decrease of mechanical parameters at Ag addition to plain HA and doped HA coatings was recognized and reported in the literature [78].

Both the doped HA coatings presented superior mechanical properties compared to the plain HA coating. Even if the best results were exhibited by the SiC-HA coating, indicative of superior adhesion to the substrate, notable plastic properties and good deformation to yielding, the Ag-SiC-HA coating also showed superior mechanical characteristics compared to the plain HA. The obtained results point to the need to use a second dopant with the HA coating when aiming to obtain bactericidal coatings containing Ag.

The coatings’ adhesion strength to the substrate was also directly measured. Figure 13 presents the obtained results. The scratch marks were evaluated using optical analysis, because this technique permits the first sign of adhesive failure (Lc1) and the normal force at which the total delamination of the coatings is produced (Lc) to be distinguished. As observed, the critical force at which the coating delamination occurs has the lowest value for the HA coating, while the highest value was measured with the Ag-SiC-HA coating. The doped HA coatings presented no sign of conformal cracks until the coating delamination (Lc), probably due to their amorphized structure, compared to the one of HA. On the contrary, the HA coating showed the first cracks at 4.1 mm, i.e., 20.5 N, and the total delamination occurring at 27.5 N. We mention that no signs of adhesive failure (Lc1) were
identified for the doped HA coatings, only the total delamination points are visible. This result might be ascribed to the amorphized structure of doped HA coatings.

![Scratch test results on HA-based coatings, at 50 N normal force.](image)

**Figure 13.** Scratch test results on HA-based coatings, at 50 N normal force.

The highest adhesion to the substrate was exhibited by the Ag-SiC-HA coating, contrary to the data deduced from the H and E values. This might be related to the lubricant property of silver producing a lubricant layer on the Ag-SiC-HA surface, determining the slide along the path of the intender, until the normal force eventually provoked the coating delamination.

Figure 14a,b present some selected images of the wear tracks on the HA coating before and at the delamination zone, and Figure 14c presents an image of the wear track on the SiC-HA coating before delamination.

![Image of the scratch tests carried out on: HA coating before the first sign of adhesive failure Lc—(a), HA coating at Lc—(b) and SiC-HA coating before Lc—(c).](image)

**Figure 14.** Image of the scratch tests carried out on: HA coating before the first sign of adhesive failure Lc—(a), HA coating at Lc—(b) and SiC-HA coating before Lc—(c).

3.5. **Tribology Tests**

The tribology tests were carried out in SBF solution at 37 ± 0.4 °C to mimic the behavior of the samples in a biological environment. The tests started after 1 h of immersion aiming to study the tribological performance of the samples with passivated surfaces, in order to exclude the influence of the passivation process on the results. Figure 15 shows the specific friction coefficients and the wear rates after the tribological tests conducted in SBF solution. Because the tribology tests were carried out in SBF, the tests began after 1 h so that the investigated samples would attain a stable, oxidized state, as observed in the corrosion tests. Although the friction coefficients and the wear rate remained at the same order of magnitude for all the investigated samples, a significant decrease of both tribological characteristics is observed for all the coated TNZT alloy compared to the bare alloy, despite the passivated surface of the bare alloy.
Figure 15. Friction coefficient and wear rate of bare and coated TNZT alloy obtained via tribology test carried out in SBF solution at 37 ± 1 °C.

Compared to the bare TNZT alloy, all coatings exhibited a lower friction coefficient and superior wear resistance. The coatings’ friction coefficients and wear rates presented a well-defined tendency, gradually decreasing at SiC and then to Ag addition. Compared to the TNZT alloy substrate, the most significant diminish was observed for the wear (about four times), compared to the friction coefficient (about three times). It should be noted that, using identical test conditions, the obtained friction coefficient values are related to the coatings’ surface roughness Ra, apart from the specific surface composition. The notable decreases of both the wear rate and friction coefficient exhibited by Ag-SiC-HA coatings are probably due to the known lubricant properties of silver. The pronounced plasticity and thermochemical stability make silver valuable in thin film solid-lubricant coatings [79].

In order to elucidate the tribological behavior of the investigated samples, one should consider the mechanical and the elasto-plastic characteristics of the samples. Usually, an augmented resistance to erosion and wear and higher elastic behavior in a surface contact is related to high H/E2 and H/E values [80]. However, there are reports affirming that predictions based on H/E or H/E2 values are less reliable if lubricated layers [81] are formed between the sliding counterparts. The measured tribological properties of Ag-SiC-HA coatings are sustaining the scratch test results, which showed that this coating presented also the highest resistance to delamination. Our experimental results show that the wear resistance of the coatings is related to the combined effects of film hardness (H), resistance to plastic deformation (H/E2) and friction characteristics (μ). However, the importance of each factor depends on the specific coating composition and microstructure.

3.6. In Vitro Evaluation of the Coatings
Cytocompatibility of Newly Developed Coatings

In vitro cytocompatibility of biomaterials is generally evaluated using a continuous established cell line. In our study, extracts obtained from the samples were tested for in vitro cytotoxicity using Vero cells using CCK8 assay. After 24 h of Vero cells cultivation in different extracts no obvious cytotoxicity was revealed by the CCK8 test; the values of absorbance corresponding to cells cultured in HA, SiC-HA, and Ag-SiC-HA-coated sample extracts were comparable to the ones cultured in the bare alloy extract and the negative control group (Figure 16a).
Figure 16. Comparative evaluation of metabolic activity of Vero cells grown for 24 h as negative control (CTR –), positive control (CTR +) and with extraction media of the analyzed samples. Results are presented as means ±SEM (n = 3) (a); phase contrast micrographs of Vero cells cultured for 24 h in standard culture medium, culture medium supplemented with 5% DMSO and in sample’s extraction media (b). Scale bar represents 200 μm.

The culture medium supplemented with 5% DMSO, which served as a cytotoxicity positive control, exhibited reduced cell viability, showing a highly toxic effect. In addition, phase-contrast microscopic cell examination indicated that test biomaterial extracts did not induce cellular morphological alterations. Thus, Vero cells displayed a typical elongated morphology and no differences in cell density were remarked, except for the positive control, where the cells lost their normal morphology and became rounded (Figure 16b). Overall, our data showed that coated materials did not release any toxic component that might affect cell morphology, viability and growth.

4. Conclusions

Hydroxyapatite (HA)-based coatings were synthesized via a RF magnetron sputtering method on Ti-10Nb-10Zr-5Ta alloy and Si substrates. The HA coating was stoichiometric and presented a typical hexagonal structure. The addition of SiC determined the amorphization of the coating. The SiC and Ag addition to the HA structure shifted the position of the peaks to lower angles, indicating cell expansion due to doping elements.

The coatings’ surfaces presented a hydrophilic character. The roughness values of the as-deposited coatings were lower than that of the bare Ti-10Nb-10Zr-5Ta (TNZT) alloy substrate, as after the corrosive attack in SBF solution the substrate was the most depreciated, while all the coatings presented lower corrosion current density values. However, the doped HA coatings presented superior corrosion resistance compared to the plain HA coating, ascribed to their amorphous structure and to the nobility of silver.

The corrosion resistance ordering of the coatings considering the corrosion current density, polarization resistance and porosity values indicated the following ranking: Ag-SiC-HA/TNZT > SiC-HA/TNZT > HA/TNZT > TNZT. The Ag-SiC-HA coating’s superior corrosion resistance against the corrosive solution was ascribed to the superior nobility induced by the presence of Ag, to the amorphous structure and to the low surface roughness presenting an almost defect-free surface, blocking the electrolyte ingress towards the substrate. The Ag-SiC-HA/TNZT coating exhibited the highest resistance polarization R_p, the smallest ion current density I_ions, the lowest porosity P and the highest protection efficiency P, closely followed by the SiC-HA/TNZT coating. All coated specimens improved the corrosion resistance of the TNZT substrate, and the Ag-SiC-HA/TNZT coating obtained via the magnetron sputtering method represents an efficient solution for the protection of metallic parts intended to be used as biomaterials.

The mechanical characteristics indicated the need to use a second dopant for HA coating when aiming to obtain bactericidal coatings containing Ag. Due to the lubricant
effect of Ag, the Ag-SiC-HA performed the best at the scratch test and during the tribology tests carried out in SBF solution.

All coatings presented a hydrophilic character, in agreement with the results obtained via in vitro cytotoxicity using Vero cells, indicating the biocompatibility of coatings, as no release of toxic components that might alter cell morphology, viability and growth was evidenced.

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