Article

Structure and Corrosion Behavior of TiO$_2$ Thin Films Deposited by ALD on a Biomedical Magnesium Alloy

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Abstract: Magnesium alloys have been investigated as temporary biomaterials for orthopedic applications. Despite their high osseointegration and mechanical (bone-like) properties, Mg alloys quickly degrade in simulated physiological media. Surface coatings can be deposited onto Mg alloys to slow the corrosion rate of these biomaterials in chloride-rich environments. TiO$_2$ films show high potential for improving the corrosion resistance of magnesium alloys. This article presents the structural observations and corrosion behavior of TiO$_2$ thin films deposited onto a MgCa$_2$Zn$_1$Gd$_3$ alloy using atomic layer deposition (ALD). Surface morphologies were observed using scanning electron microscopy (SEM) and atomic force microscopy (AFM), and Raman analysis of the deposited TiO$_2$ films was also carried out. The corrosion behavior of the uncoated alloy and the alloy coated with TiO$_2$ was measured in Ringer’s solution at 37 °C using electrochemical and immersion tests. The microscopic observations of the TiO$_2$ thin films with a thickness of about 52.5 and 70 nm showed that the surface morphology was homogeneous without visible defects on the TiO$_2$ surface. The electrochemical and immersion test results showed that the thin films decreased the corrosion rate of the studied Mg-based alloy, and the corrosion resistance was higher in the thicker TiO$_2$ film.

Keywords: titanium dioxide thin films; surface morphology; electrochemical studies; immersion tests; corrosion behavior

1. Introduction

Magnesium plays an essential role in human metabolism and forms one of the most important intracellular cations. Mg can form chelates with cell membrane phospholipids, affecting their structural stability and allowing the cell to better fulfill its protective functions. More than 53 percent of total bodily magnesium is located in human bones.

Magnesium alloys are widely used in medicine because of their many suitable properties, e.g., high mechanical strength, lightweight, etc. [1]. They are also nontoxic and biocompatible, but magnesium is one of the most electrochemically active metals [2]. Hence, the anticorrosion properties of magnesium alloys are very poor, and their high biodegradation rate affects cell viability and cellular functions. Thus, it is necessary to modify the surface of these materials. TiO$_2$ thin films can be used to modify magnesium alloy surfaces. This oxide exists in three crystal structures: anatase, brookite, and rutile. Rutile is rarer and much more difficult to prepare. From an application perspective, anatase and rutile are very important structures. Moreover, their properties were studied much more often than those of brookite. It can be stated that rutile is the most significant crystalline structure for bone tissue mineralization. However, rutile shows no advantages in in vitro experiments over anatase. Moreover, anatase may increase the adhesion and proliferation of osteoblasts.

TiO$_2$ films have been widely used due to their many suitable properties, such as anticorrosion, mechanical, and antibacterial properties. TiO$_2$ has also been used in dental and orthopedic applications. Some investigations have used TiO$_2$ composite coatings on...
Mg-based alloys [3,4]. Bakhsheshi-Rad et al. [3] deposited a TiO$_2$ coating onto a MgCa alloy using a micro-arc oxidation method. Then, a zinc-doped hydroxyapatite coating was deposited onto TiO$_2$ using electrophoretic deposition. The authors studied the antibacterial activity of the composite coating against *Escherichia coli*, and the coating showed good antibacterial properties. The cytotoxicity tests indicated that the osteoblast cell viability cultured with a zinc-doped coating was higher than TiO$_2$, but the titanium dioxide coating protected against *E. coli* [3]. Fu et al. [5] studied anatase TiO$_2$ fabricated by a sol–gel method. The TiO$_2$ nanoparticles were then covered by gold, and the antibacterial activity of these nanocomposite coatings was investigated using two types of bacteria (*Escherichia coli* and *Bacillus megaterium*). The authors confirmed the biocidal effect of the TiO$_2$ coatings.

Many reports present the biomedical uses of TiO$_2$ films with different thickness deposited onto different substrates (particularly Ti-based substrates) by an atomic layer deposition (ALD) process [6,7]. Nazarov et al. [6] studied the effect of combining three complementary methods, such as severe plastic deformation (SPD), chemical etching (CE), and atomic layer deposition (ALD). The aim of SPD was to improve mechanical properties. CE was used for preparation of a morphology and topography necessary for implant osseointegration. TiO$_2$ coatings (with a thickness in the range of 350–1000 nm) were deposited on the nanostructured (UFG—ultrafine grained) titanium rods by the ALD method. The obtained results of in vitro investigations indicated an improvement in all parameters, e.g., viability, proliferation, alkaline phosphatase (ALP), etc. The authors stated that this was caused by the change in the surface composition and the anatase structure of the TiO$_2$ films. The crystalline structure of the films affects the osseointegration of the bone tissue.

Matola et al. in their work [7] studied TiO$_2$ coatings (with a thickness of about 0.275 and 8.25 nm) deposited onto Ti sheets and titanium dioxide nanotubes (TNT) layers using ALD. It was noted that the thinner TiO$_2$ coating significantly improved cell growth on different substrates. The cell growth of WI-38 fibroblasts was improved 50% on TNT layers and Ti sheets; SH-SY5Y neuroblast and MG-63 osteoblast cell growth was increased by 30% on TNT layers coated with 0.75 nm thick TiO$_2$ ALD compared to the uncoated substrates.

Many works have also indicated that TiO$_2$ coatings improve the corrosion resistance of magnesium alloys [8–11]. Hu et al. [9] studied TiO$_2$ deposited onto AZ31 alloys and stated that the ceramic films decreased the corrosion rate of magnesium alloys. Li et al. [10] investigated a TiO$_2$ coating obtained by a sol–gel method and confirmed that the coating significantly improved the corrosion behavior of the Mg-Ca alloy in simulated body fluid (SBF). The electrochemical results showed that the corrosion current density, $i_{corr}$, of the obtained coating was three times lower than that of the studied alloy. White et al. [11] also studied the effect of a TiO$_2$ coating deposited on an AZ31 magnesium alloy on its corrosion behavior. Samples were tested in 3.5 wt.% NaCl solution, and the results showed that the plasma electrolytic oxidation (PEO) of TiO$_2$ decreased the corrosion rate compared with the uncoated alloy. The corrosion rates of the AZ31 alloy and the TiO$_2$ were $5.6 \times 10^{-2}$ and $6.047 \times 10^{-6}$ mm year$^{-1}$, respectively.

As mentioned above, different techniques can be used to deposit TiO$_2$ films, e.g., sol–gel, plasma electrolytic oxidation, magnetron sputtering, chemical vapor deposition (CVD), etc. PEO technology is mainly used for the deposition of oxide coatings on the surface of light alloys, such as titanium, aluminum, and magnesium [12]. Many researchers produce and study nanocomposite coatings using this method [13,14]. However, one of the most promising deposition methods is atomic layer deposition, which is a variation of CVD that allows for the deposition of nanostructured thin films [15,16]. ALD is a chemical process that produces ultrathin coatings on highly non-uniform and non-planar surfaces [16,17]. Therefore, ALD largely contributes to many advanced nanotechnologies. It should also be noted that this method is successfully used in a lot of industrial and research applications. ALD films with a precise controlled thickness are deposited onto all kinds of substrates through repetition of ALD cycles [18]. The growth rate of ALD is related to the flux of the precursor on the substrate. ALD is particularly effective in coating the surfaces for...
topography with a very high aspect ratio and also requiring the surface of the multilayer film to have a good quality interface.

ALD has some advantages, such as precise thickness control, a low growth temperature, strong bonding strength, large-area uniformity, etc. Moreover, the low thickness of deposited coatings shows good adhesion to the substrate, making this method better than other techniques, such as PVD (physical vapor deposition) and sol-gel methods.

For the deposition of TiO$_2$ thin films using ALD, different precursors are used, e.g., titanium isopropoxide, titanium tetrachloride, tetrakis(dimethylamino)titanium (TDMATi), alkoxides, such as Ti(OMe)$_4$, Ti(OEt)$_4$, and Ti(OiPr)$_4$ in combination with H$_2$O, oxygen, or ozone [15]. One of the most widely studied ALD of TiO$_2$ processes is that using TiCl$_4$ with H$_2$O. Early study on the ALD of TiO$_2$ using TiCl$_4$ and water as reactants with growth temperatures from 150 to 600 °C was conducted by Ritala et al. [19]. In this work, the effect of the substrate material on the crystal structure and growth rate was presented.

This article presents the results of the structural observations and corrosion behavior of TiO$_2$ thin films with a thickness of about 52.5 and 70 nm, deposited onto a MgCa$_2$Zn$_1$Gd$_3$ alloy using ALD. Moreover, we assessed whether the slight difference in the TiO$_2$ film thickness improved the corrosion resistance of the studied alloy.

2. Materials and Methods

The MgCa$_2$Zn$_1$Gd$_3$ alloy was prepared using high-purity magnesium (99.99%), calcium (99.5%), zinc (99.99%), and gadolinium (99.9%). The alloy was cast in an induction furnace at 750 °C using Ar as the protective gas. Samples of the cast alloy were in the form of cylinders with diameters of 13 mm and heights of 5 mm. Before the ALD process, surfaces of the samples were mechanically polished with SiC paper, from grade 500 to 4000, and polished with a diamond suspension. Finally, the samples were ultrasonically degreased in acetone for 15 min, cleaned in alcohol, and washed with distilled water.

The TiO$_2$ thin films were deposited on a MgCa$_2$Zn$_1$Gd$_3$ alloy substrate by ALD using an R-200 system from Picosun (Espoo, Finland). As a precursor of TiO$_2$, titanium tetrachloride (TiCl$_4$) was used, which reacted with water to enable the deposition of thin films. Protective thin films were deposited after 1500 and 2000 cycles at 250 °C, with thicknesses of 52.5 and 70 nm, respectively. These values resulted from the number of deposition cycles, where one deposition cycle produced a 0.035 nm-thick film. The technological conditions of the ALD method selected on the basis of preliminary tests are presented in Table 1.

| Table 1. The technological conditions of the atomic layer deposition (ALD) method selected on the basis of preliminary tests. |
| --- |
| TiCl$_4$ | Carrier Gas Flow Rate (N$_2$), sccm | 150 |
| | Precursor introduction time, s | 0.2 |
| | Chamber flushing time, s | 5.0 |
| H$_2$O | Carrier gas flow rate (N$_2$), sccm | 200 |
| | Reagent introduction time, s | 0.2 |
| | Chamber flushing time, s | 5.0 |
| Substrate temperature, °C | 250 |
| Number of cycles | 1500–2000 |

The thickness of the TiO$_2$ films was assessed with an alpha spectroscopic ellipsometer (SE) from Woollam (Lincoln, OR, USA). In this method, the linearly polarized light reflects from the sample surface, becomes elliptically polarized, and travels through a continuously rotating polarizer (referred to as the analyzer). The amount of light allowed to pass will depend on the polarizer orientation relative to the electric field “ellipse” coming from the sample. The detector converts light to electronic signal to determine the reflected polarization. This piece of information is compared to the known input polarization to
determine the polarization change caused by the sample reflection. This is the ellipsometry measurement of $\psi$ (the ratio of the amplitude diminutions) and $\Delta$ (the phase difference induced by the reflection). The measurements were carried out at room temperature under angles 65°, 70°, and 75°. The $\psi$ and $\Delta$ measurements were performed on pure polished substrate in the first step and on substrate with deposited thin film in the further step. The thickness value was determined with software based on one used model. The used model included several layers (substrate/native oxide/TiO$_2$/air), where the parameters of individual layers were fitted step by step (in the first step just for the substrate and in the second step for the substrate with the deposited film). The thin film of TiO$_2$ was fitted with a Cauchy layer.

Observations of the surface morphology were carried out using a Zeiss SEM (SUPRA 35 model; electron high tension (EHT) = 3.0, 5.0 and 10.0 kV, SE mode, in-lens detector; EHT = 20.0 kV, QBSD detector, Zeiss, Thornwood, NY, USA) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector. The components of the samples’ surface after corrosion tests have been identified by EDS analysis.

Structure identification of the thin films was carried out using a Raman spectrometer (inVia Reflex model) from Renishaw (New Mills, UK), which was equipped with an argon-ion laser with a wavelength of 514.5 nm. It was calibrated before each set of measurements using the Si line at 520 cm$^{-1}$ as a reference.

Electrochemical corrosion studies were carried out using an Autolab PGSTAT302N Multi BA potentiostat (Metrohm AG, Herisau, Switzerland). The experiment was performed in Ringer’s solution (8.6 g·dm$^{-3}$ NaCl, 0.3 g·dm$^{-3}$ KCl, 0.48 g·dm$^{-3}$ CaCl$_2$·6H$_2$O) at 37 °C. The scan rate of the corrosion potential was 1 mV·s$^{-1}$. Before measurements, samples were immersed in Ringer’s solution for 5 min for stabilization. The corrosion parameters (e.g., corrosion potential, $E_{corr}$; corrosion current density, $i_{corr}$; and corrosion polarization resistance, $R_p$) were determined using Tafel plot analysis.

The corrosion behavior of the nano TiO$_2$ films was also observed using immersion tests in Ringer’s solution at 37 °C for 24 h. The studies provided an estimation of the gas corrosion product (H$_2$ evolution volume). For the measurements, cylindrical samples with a testing area of 1.1 cm$^2$ were prepared. The volume of evolved hydrogen was measured by taking into account the frontal area of the samples.

After immersion tests, the corroded surfaces of the MgCa2Zn1Gd3 alloy samples with TiO$_2$ thin films were investigated by Raman spectroscopy and observed using SEM and AFM. To remove the corrosion products, samples were rinsed with distilled H$_2$O and immersed in CrO$_3$ solution before observations.

3. Results and Discussion

The TiO$_2$ thin films with a thickness of about 52.5 and 70 nm were deposited onto the MgCa2Zn1Gd3 alloy using an ALD technique after 1500 and 2000 deposition cycles, respectively.

Observations carried out using SEM showed that the MgCa2Zn1Gd3 alloy showed a dendritic microstructure (Figure 1) [20]. It can also be observed that the surface morphology of both TiO$_2$ films was homogeneous and uniform (Figure 2). The grains displayed elongated shapes in the TiO$_2$ film deposited after 1500 cycles, and a more spherical shape for the film after 2000 deposition cycles (Figure 2a,b). In both cases, the grain boundaries were strictly defined, and the TiO$_2$ surface did not present defects, such as cracks and pores (Figure 2c,d) [21]. The film grains, which are important during corrosion processes [22], form agglomerates. A denser and more uniform film decreased the corrosion rate.
The film grains, which are important during corrosion processes [22], form agglomerates. A denser and more uniform film decreased the corrosion rate.

**Figure 1.** SEM image of the MgCa2Zn1Gd3 alloy.

**Figure 2.** SEM images of the surface morphology of the TiO2 thin films deposited after: (a,c) 1500 and (b,d) 2000 cycles onto the MgCa2Zn1Gd3 alloy by ALD.

Measurement of the thickness and refractive index was performed using a spectroscopic ellipsometer. The used spectral range was 300–900 nm. The samples were measured at a fixed angle of incidence of $\varphi = 65^\circ$, 70°, and 75°. Figure 3 shows the measured and modeled ellipsometric spectra of TiO$_2$ deposited with 1500 and 2000 cycles, respectively. The model fits the measurement excellently. The thickness is equal to 52.55 and 70.00 nm, respectively (Table 2).

**Table 2.** Refractive index and thickness of the TiO$_2$ thin films.

| Sample          | Thickness, $d$, nm | Refractive Index, $n$, nm |
|-----------------|--------------------|--------------------------|
| TiO$_2$ (1500 cycles) | 52.5               | 2.41                     |
| TiO$_2$ (2000 cycles) | 70.00              | 2.42                     |

ALD can be used to grow anatase TiO$_2$ at lower temperatures than other techniques [23], and this crystal structure may appear when TiO$_2$ film growth temperatures exceed 165 °C [24]. Aarik et al. studied TiO$_2$/ALD films using TiCl$_4$ as the precursor and water as the oxygen source [25]. They stated that TiO$_2$ films grown below 165 °C were amorphous and those deposited in the range of 165–350 °C contained the anatase phase.
Figure 3. Measured and modeled ellipsometric spectra ($\varphi = 65^\circ$, $70^\circ$, and $75^\circ$) of TiO$_2$ thin films deposited with 1500 (a,b) and 2000 (c,d) cycles.

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Raman analysis confirmed the crystalline structure of the thin films. The Raman spectra of the TiO$_2$ films showed characteristic bands of an anatase structure (144, 395, 517, 636 cm$^{-1}$, and 196 cm$^{-1}$ for the 70 nm-thick film) (Figure 4). These were in agreement with other Raman spectra for anatase TiO$_2$ films [23,26]. Anatase TiO$_2$ has a tetragonal crystal structure with a space group of I4$_1$/amd (space group no. 141) with the following lattice parameters: $a = 3.784$ Å, $b = 3.784$ Å, and $c = 9.515$ Å. For anatase, there exists 15 optical modes with the normal vibrations: $1A_{1g} + 1A_{2u} + 2B_{1g} + 1B_{2u} + 3E_g + 2E_u$. Six of the modes represented by $1A_{1g}$, $2B_{1g}$, $3E_g$ symmetries are Raman active. The $E_g$ Raman modes are mainly associated with the symmetric stretching vibration. The $B_{1g}$ Raman modes are mainly associated with the symmetric bending vibration and the $A_{1g}$ with the anti-symmetric bending vibration of O–Ti–O [27].

Figure 4. Raman spectra of the TiO$_2$ thin films deposited after: (a) 1500 and (b) 2000 cycles onto MgCaZn1Gd3 alloy by ALD.
The surface topography of the oxide films and the MgCa2Zn1Gd3 alloy was observed using AFM (Figures 5 and 6).

![AFM images](image1.png)  
**Figure 5.** The 3D atomic force microscopy (AFM) image (a) and 2D AFM image (b) of the surface topography of the MgCa2Zn1Gd3 alloy.

![AFM images](image2.png)  
**Figure 6.** The 3D AFM images (a,b) and 2D AFM images (c,d) of the surface topography of the TiO2 thin films deposited onto the MgCa2Zn1Gd3 alloy after: (a,c) 1500 cycles; (b,d) 2000 cycles.

The observation results were in agreement with the SEM results, which showed that both TiO2 thin films have a granular structure (Figure 6) [23,26]. It seems that particle aggregation decreased as the number of deposition cycles increased.

The roughness parameters (RMS, root mean square; Ra, average roughness) were similar after different numbers of deposition cycles (Table 3).
The corrosion degradation of Mg and its alloys is too fast, so it is difficult to estimate the time of implant failure. Alloying is one of the methods for decreasing the corrosion rate of magnesium alloys, but many elements have a low solubility in a Mg matrix. Therefore, the deposition of coatings (without pores and cracks and which have good adhesion to the substrate) onto Mg alloys is highly interesting [28–30], and it seems that ALD is a good technique for depositing TiO$_2$ thin films to protect MgCa$_2$Zn$_1$Gd$_3$ from corrosion.

Electrochemical tests were performed in Ringer’s solution at 37 °C after a stabilization time of 5 min. The corrosion results are presented in the form of potentiodynamic curves for both TiO$_2$ thin films and the MgCa$_2$Zn$_1$Gd$_3$ alloy. The polarization curves of the oxide films have similar shapes but slightly different corrosion potentials ($E_{\text{corr}}$). The results of the corrosion studies show that $E_{\text{corr}}$ of the TiO$_2$ films after different numbers of deposition cycles shifted to more positive values. This suggests an improved corrosion resistance of the uncoated alloy (Figure 8). It can be stated that the TiO$_2$ films deposited by ALD decreased the corrosion rate of the magnesium alloy during electrochemical tests [28].

### Table 3. Roughness parameters of the TiO$_2$ films applied and the MgCa$_2$Zn$_1$Gd$_3$ alloy.

| Sample                   | Roughness Average, $R_a$, nm | Root Mean Square, RMS, nm |
|-------------------------|------------------------------|--------------------------|
| MgCa$_2$Zn$_1$Gd$_3$    | 4.91                         | 5.68                     |
| TiO$_2$ (52.5 nm thick) | 13.22                        | 16.66                    |
| TiO$_2$ (70 nm thick)   | 14.34                        | 18.42                    |

A comparison of the obtained results indicates that surface irregularities for both TiO$_2$ films did not exceed 40 nm (Figure 7).

**Figure 7.** Histogram of the height distribution for the TiO$_2$ films deposited onto MgCa$_2$Zn$_1$Gd$_3$ alloy after: (a) 1500 cycles; (b) 2000 cycles.

**Figure 8.** Polarization curves of the TiO$_2$ thin films with thicknesses of 52.5 and 70 nm, and the MgCa$_2$Zn$_1$Gd$_3$ alloy in Ringer’s solution at 37 °C.
Tafel extrapolation of the polarization curves allows the polarization resistance ($R_p$) and corrosion current density ($i_{corr}$) to be determined. The results of Tafel extrapolation are presented in Table 4. It should be noted that the corrosion potential indicates the corrosion resistance of the studied material, while $i_{corr}$ is proportional to its corrosion rate.

**Table 4.** Corrosion parameters of 52.5 and 70 nm-thick TiO$_2$ films and the MgCa2Zn1Gd3 alloy.

| Sample                  | Corrosion Potential, $E_{corr}$, V | Polarization Resistance, $R_p$, $\Omega$·cm$^2$ | Corrosion Current Density, $i_{corr}$, $\mu$A·cm$^{-2}$ |
|-------------------------|----------------------------------|-----------------------------------------------|-------------------------------------------------------|
| MgCa2Zn1Gd3             | $-1.51 \pm 0.03$                | 420 ± 7                                        | 148 ± 4                                               |
| TiO$_2$ (52.5 nm thick)  | $-1.50 \pm 0.03$                | 445 ± 6                                        | 126 ± 3                                               |
| TiO$_2$ (70 nm thick)    | $-1.47 \pm 0.03$                | 479 ± 8                                        | 95 ± 3                                                |

The MgCa2Zn1Gd3 alloy with a 52.5 nm-thick TiO$_2$ film has a slightly higher $E_{corr}$ ($-1.50$ V) and $i_{corr}$ (126 $\mu$A·cm$^{-2}$) than the second film ($E_{corr}$ of the studied alloy with a thicker film was $-1.47$ V, and $i_{corr}$ was 95 $\mu$A·cm$^{-2}$). It can be expected that the slightly thicker film will show a higher corrosion resistance. This result was not in agreement with the roughness measurements, where the RMS and $R_a$ values of this film were higher than the 52.5 nm-thick TiO$_2$ film. Gawlik et al. [1] stated that in some cases, the roughness does not influence the degradation rate of coated alloys [11]. The polarization resistance of the MgCa2Zn1Gd3 alloy with a thinner TiO$_2$ film was 445 $\Omega$·cm$^2$, while the thicker film reached an $R_p$ value of 479 $\Omega$·cm$^2$.

Marin et al. [28] deposited TiO$_2$/aluminum coatings onto an AZ31 alloy using ALD, and the results showed that ALD produced coatings that protected the magnesium alloy from corrosion in aqueous NaCl solutions. It has also been reported that ALD should be used when less material is needed to achieve a high corrosion resistance of Mg alloys [29].

The corrosion behavior of both TiO$_2$ thin films and the MgCa2Zn1Gd3 alloy was also observed using 24 h immersion tests in Ringer’s solution at 37 °C. The immersion tests allow the measurement of the corrosion product, i.e., the hydrogen evolution volume. Some studies have provided information about the real corrosion behavior of magnesium alloys. Witte et al. [31] stated that the maximum hydrogen evolution rate tolerable by the human body is 0.068 mL·cm$^{-2}$·day$^{-1}$, but Song et al. [32] reported that the maximum H$_2$ evolution is 0.01 mL·cm$^{-2}$·day$^{-1}$. Figure 9 presents the H$_2$ evolution volume during 24 h of immersion for the studied TiO$_2$ thin films deposited onto the MgCa2Zn1Gd3 alloy.

![Figure 9.](image-url) Hydrogen evolution volume as a function of immersion time in Ringer’s solution at 37 °C for 24 h for the studied TiO$_2$ thin films deposited onto the MgCa2Zn1Gd3 alloy and uncoated alloy.
The H$_2$ evolution volume (9.67 mL cm$^{-2}$) was higher for the studied alloy with a thin film deposited after 1500 cycles (52.5 nm thick). The thicker TiO$_2$ film had a slightly lower hydrogen evolution volume of 5.68 mL cm$^{-2}$, while the MgCa2Zn1Gd3 alloy displayed a higher hydrogen evolution volume of 17.58 mL cm$^{-2}$. These results suggest an improved corrosion resistance for the thicker film, which is important for materials for orthopedic applications.

The corrosion rates, $v_{\text{corr}}$, of the MgCa2Zn1Gd3 alloy with a TiO$_2$ coating, calculated from the hydrogen evolution volume after 24 h of immersion were 3.38 and 2.62 mm year$^{-1}$ for the 52.5 and 70 nm-thick films, respectively. The $v_{\text{corr}}$ of the uncoated alloy was 6.15 mm year$^{-1}$. After the immersion tests, the samples coated with TiO$_2$ thin films were observed by SEM (Figure 10).

![SEM images of corroded samples with TiO$_2$ thin films deposited onto the MgCa2Zn1Gd3 alloy after 1500 cycles: (a,c,e), and 2000 cycles: (b,d,f) after 24 h of immersion in Ringer’s solution at 37 °C.](image)

Figure 10. SEM images of corroded samples with TiO$_2$ thin films deposited onto the MgCa2Zn1Gd3 alloy after 1500 cycles: (a,c,e), and 2000 cycles: (b,d,f) after 24 h of immersion in Ringer’s solution at 37 °C.

Lamellar-shaped and needle-like corrosion products were visible on the alloy substrate (Figure 10a,b), which were probably magnesium chlorides. The results of the EDS analysis...
after corrosion tests indicated that the corrosion products contained Mg, O, and Cl for the MgCa2Zn1Gd3 alloy with a 70 nm-thick film. Besides these, Zn and C were observed in the alloy with a 52.5 nm-thick TiO2 film (Figure 11), which were probably from zinc oxides and carbonates [11].

Chloride ions in Ringer’s solution break down the Mg(OH)2 film and accelerate the corrosion of the studied MgCa2Zn1Gd3 alloy by forming MgCl2. The corrosion products did not cover the entire surface of the samples, as seen in Figure 10c,d. After the removal of corrosion products, the grain boundaries were visible (Figure 10e,f). It can be observed that microcracks usually propagated along grain boundaries.

Moreover, the corroded samples of the MgCa2Zn1Gd3 alloy with 52.5 and 70 nm-thick TiO2 films were characterized by Raman spectroscopy, and the obtained results indicated the presence of the TiO2 on the surface of the studied alloy (Figure 12). These results suggest that both TiO2 films are durable, and corrosion did not attack the entire surface of the oxide films.

The topography of the MgCa2Zn1Gd3 alloy with thin films after immersion tests was also observed using AFM (Figure 13).
Figure 13. The AFM images of the 3D rendering of the TiO$_2$ surface topography after 24 h of immersion in Ringer’s solution at 37 °C: (a) 52.5 nm-thick TiO$_2$ film and (b) 70 nm-thick TiO$_2$ film.

As seen in Figure 13, the topographies of both thin films were similar, and no cracks were visible. It is well known that surfaces prone to corrosion have a topography with many cavities. Based on this, it can be assumed that the studied alloy with a 52.5 nm-thick TiO$_2$ film was slightly more susceptible to corrosion. The roughness parameters of the MgCa2Zn1Gd3 with TiO$_2$ films confirmed that the thicker film was slightly more corrosion-resistant than the thinner one. The average roughness of the alloy with a 52.5 nm-thick film was 295.1 nm, while for the second one, the $R_a$ was 273.05 nm. The values of RMS were 372.2 and 335.47 nm for the 52.5 and 70 nm-thick films, respectively.

4. Conclusions

In this article, the structure and corrosion behavior of the TiO$_2$ thin films deposited onto the MgCa2Zn1Gd3 alloy using the ALD method were investigated. The results of our work indicated that 52.5 and 70 nm-thick TiO$_2$ films had homogeneous structures, and their grains had similar dimensions. The TiO$_2$ surface topography observations performed using AFM were in agreement with the SEM results, and showed that these films have a granular structure. Both TiO$_2$ films have an anatase structure, which is more biologically active than rutile or brookite [18].

We carried out the electrochemical and immersion tests in Ringer’s solution, simulating the human physiological environment at 37 °C. As was mentioned above, Mg alloys and also the studied MgCa2Zn1Gd3 alloy are characterized by poor corrosion resistance in such a chloride-rich environment. In this respect, it should be noted that the substrate and corrosion environment influence the corrosion behavior of the studied TiO$_2$ films. Based on the corrosion test results, we showed that the TiO$_2$ films deposited onto MgCa2Zn1Gd3 effectively protect this alloy from corrosion. Moreover, the 70 nm-thick TiO$_2$ film was slightly more corrosion-resistant than the thinner one. After 24 h of immersion in an aggressive environment, the presence of TiO$_2$ on the surface of the alloy was indicated by Raman analysis. This suggests that the corrosion products did not cover the entire surface of the studied samples. The low thickness and high purity of the applied films make ALD an excellent corrosion-inhibiting method compared with other techniques, such as sol–gel or PVD.

In recent years, ALD has been actively used to modify the surface of biomaterials, but in the literature, there are not so many reports on the application of ALD coatings (e.g., TiO$_2$ coatings) on orthopedic implants made of biodegradable materials, such as Mg-based alloys. The results presented in our work open the way to modification of the surface of Mg-based alloys using the ALD method not only with TiO$_2$ films, but also with other oxides, in order to increase the corrosion resistance and biocompatibility of these materials.

In the future, the authors plan to produce and investigate the ALD of TiO$_2$ and ZnO films with smaller thicknesses than those presented in the article.
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