Synthesis and biodegradation evaluation of nano-Si and nano-Si/TiO$_2$ coatings on biodegradable Mg–Ca alloy in simulated body fluid

H.R. Bakhsheshi-Rad$^{a,*}$, E. Hamzah$^a$, M. Daroonparvar$^a$, M. Kasiri-Asgaram$^b$, M. Medraj$^c$

$^a$Department of Materials, Manufacturing and Industrial Engineering, Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia
$^b$Materials Engineering Department, Najafabad Branch, Islamic Azad University, Najafabad, Isfahan, Iran
$^c$Department of Mechanical Engineering, Concordia University, 1455 De Maisonneuve Blvd. West, Montreal, Canada QC H3G IM8

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Abstract

In the present study, nano-Si and nano-Si/TiO$_2$ composite coatings have been successfully synthesized on the surface of Mg–1 wt%Ca alloy by the physical vapor deposition (PVD) method. The surface morphology and compositions of the coated specimens were characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The results show the formation of thin and compact coating layers which homogeneously cover the surface of Mg alloy. Some micro-pores and micro-cracks were observed in the Si and Si/TiO$_2$ films. It was also found that the Si and TiO$_2$ nanoparticle had a spherical morphology with an average particle size of 30–40 nm and 70–80 nm, respectively. Electrochemical studies revealed that nano-Si/TiO$_2$ coating offers a significant reduction in the corrosion rate (0.57 mm/year) compared to the Si coated (0.91 mm/year) and the uncoated alloys (6.21 mm/year) in simulated body fluid (SBF). Hydrogen evolution studies showed a lower degradation rate of nano-Si/TiO$_2$ (1.57 ml/cm$^2$/day) than that of nano-Si coated alloy (2.22 ml/cm$^2$/day). Immersion test showed that the nano-Si/TiO$_2$ coating presented a greater nucleation site of hydroxyapatite (HA) than the uncoated sample. Thus nano-Si/TiO$_2$ composite coating prepared by PVD on the Mg–Ca alloy is more appropriate for biomedical applications.

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1. Introduction

Magnesium alloys as biodegradable materials have drawn much interest due to eliminating the need for a second surgery to remove the biomedical implants [1,2]. Mg-based biomaterials have inevitable roles in human metabolism, good biocompatibility, and superior mechanical properties [3,4]. However, clinical applications of Mg are limited due to its relatively poor corrosion resistance, rapid degradation rate and hydrogen gas evolution in the human body fluid [5–7]. The deposition of coatings by physical vapor deposition (PVD) is an effective method to overcome these drawbacks and enhance the corrosion resistance of these alloys [8]. In addition, PVD is a clean environmental friendly technique, and does not produce wastes or appreciable atmospheric emissions. There are several studies related to the surface modifications of magnesium alloys by TiN, CrN, and AlN PVD coatings and their protection ability against corrosion [9,10]. In this study, silicon coating was selected because it is an essential ion in osteogenic cells and due to its biocompatibility, bioinert nature to biological tissues and more importantly, silicon deficiency can cause abnormal bone growth [1,2,11]. Titania (TiO$_2$) is also a non-toxic and chemically stable material that can be used to improve the biocompatibility of the substrate [12]. However, studies on preparation and characterization of nano-Si and nano-Si/TiO$_2$ on magnesium alloy by the physical

*Corresponding author. Tel.: +0060 147382258.
E-mail addresses: rezabakhsheshi@gmail.com, bhamidreza2@live.utm.my (H.R. Bakhsheshi-Rad).

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vapor deposition technique could not be found in the literature. Therefore, in the present study, PVD is utilized to fabricate nano-Si and nano-Si/TiO₂ composite coatings and elaborate their surface characteristics and in-vitro corrosion behavior.

2. Experimental details

Pure magnesium (99.98% Mg), and Mg–32%Ca master alloy were used to prepare magnesium alloy containing 1 wt% Ca. In preparation for further experiments, several Mg–1%Ca specimens, with dimensions of 20 mm × 15 mm × 10 mm, were cut from the ingot. Then, they were mechanically wet ground with 320–2000 SiC grit papers until all visible scratches were removed. A hybrid ion beam deposition system, consisting of a linear ion source and a magnetron sputtering source, was selected to deposit the coatings on the substrates. The Mg alloys were ultrasonically washed in pure alcohol for 5 min before placement inside the vacuum chamber. An ion source with Ar gas was used to clean the surface of the Mg alloys for 40 min. This pre-treatment was performed, when the base pressure of the chamber was below 4 × 10⁻³ Torr. Physical vapor deposition was performed at room temperature with argon and oxygen as the sputtering gases. It should be noted that Ar gas was used for the Si layer and that both oxygen and argon gases were employed for TiO₂ as a second layer. The PVD parameters are as follows: a working pressure of 8 × 10⁻³ Torr, a radio frequency (RF) power of 200 W, a deposition time of 90 min and a bias voltage of −150 V. An X-ray diffractometer (Siemens-D5000) was used to identify the various phases, using Cu-Kα radiation (λ = 1.5405 Å) generated at 35 kV and 25 mA. Fourier-transform infrared (FTIR) spectroscopy was used to determine the surface functional groups of the coated sample. The FTIR spectrum was recorded in a spectral range of 4000–350 cm⁻¹. Microstructural observation was performed using a scanning electron microscope (SEM, JEOL JSM-6380LA), equipped with an EDS and a transmission electron microscope (TEM, HT7700 Hitachi). Rectangular specimens, with a surface area of 1 cm², were mounted on epoxy resin for electrochemical tests. The test was conducted at 37 °C in an open air glass cell containing 350 ml Kokubo solution with a pH of 7.4, using PARSTAT 2263 potentiostat/galvanostat (Princeton Applied Research). A three-electrode cell was used for potentiodynamic polarization tests. The reference electrode was a saturated calomel electrode (SCE), the counter-electrode was made of graphite rod, and the specimen was the working electrode. All experiments were carried out at a constant scan rate of 0.5 mV/s, initiated at −250 mV below the open-circuit potential. For compression test, cylindrical specimens with a diameter of 10 mm and a height of 20 mm were immersed in SBF for 10 days, and then cleaned in a boiling solution of chromium trioxide (CrO₃) to remove the surface corrosion product. The specimens were then dried in warm air. Compression tests were performed using an Instron-5569 universal testing machine at a displacement rate of 1.0 mm/min, at an ambient temperature. For each testing material, two specimens were examined. The immersion test procedure was carried out based on the ASTM:

Fig. 1. SEM images of the surface of (a, d) uncoated Mg alloy; (b, e) Si coated; (c, f) Si/TiO₂ coated and EDS analysis of (g) point A; (h) point B and (k) point C.
The specimens were then immersed in a beaker containing 200 ml of Kokubo simulated body fluid (SBF). The average pH value of the SBF from three measurements was recorded during the soaking experiment after every 12 h interval. The hydrogen evolution rate was also measured during the 168 h immersion in the Kokubo solution experiment. A sample was immersed in a beaker covered with a funnel to collect evolved hydrogen in a burette above the funnel. The hydrogen evolution rate was calculated in ml/cm²/day before renewing the solution and the volume of hydrogen was measured with a scaled burette.

3. Results and discussion

3.1. Microstructure and composition

Fig. 1 shows SEM images of the uncoated, Si and Si/TiO₂ coated specimens. Fig. 1a and d shows that the microstructure of uncoated Mg–Ca consisted of α-Mg and small amount of Mg–Ca secondary phases. The secondary phases are in the form of eutectic structure (α-Mg+Mg₂Ca) along the grain boundary. The corresponding EDS analysis suggests that the marked area is composed of Mg and Ca indicating the formation of Mg₂Ca compound (Fig. 1g). The surface of Si and Si/TiO₂ coatings is composed of spherical particles in the nano scale, as can be seen in (Fig. 1b, c, e and f). It was reported that the type of resulting phases and their morphology depend on the coating method and the operating conditions [2,13]. The results of the EDS analysis of Si-coated sample showed that the coating is composed of Mg, Ca, O and Si (Fig. 1h). Mg and Ca are from the substrate. On the other hand, the main elements in the Si/TiO₂ coating are Ca, O, Mg, Si and Ti indicating again that the Mg and Ca peaks are from the substrate (Fig. 1k). Fig. 2 shows cross-sectional SEM image and the corresponding EDS line scans of the nano-Si and nano-Si/TiO₂ composite coated specimens, indicating formation of thin and compact coating layers which homogeneously cover the surface of the Mg alloy. The thickness of the Si and Si/TiO₂ coating is around 1.20 μm and 1.80 μm, respectively. There is a sound adhesion between the deposited coating and the underlying substrate (Fig. 2a and d). However, there are some micro-pores and micro-flaws in the film, but the microstructure of the Si/TiO₂ coating is denser than that of the Si coating. Therefore, the presence of TiO₂ reduces the occurrence of pores and cracks in the Si coating. The line scanning of elements distribution across the Si and Si/TiO₂ coatings are exhibited in Fig. 2c and f. Mg and Ca peaks are from the substrate due to the relatively large electron beam interaction volume compared to the coating thickness, while Si can be detected at the coating/substrate interface and O contents steadily increase from substrate toward the coating (Fig. 2c). Furthermore, noticeable increase in Ca counts towards the substrate in Si coated sample might be due to encountering Mg₂Ca precipitate in the scan. The presence of O element in the spectrum is due to a presumed reaction between the atmospheric oxygen or moisture with the dangling bonds.
and after exposing the film to the atmosphere [11]. However, in the Si/TiO2 coating, at the vicinity of the coating/substrate interface, the Si and Ti content gradually increases from the substrate toward the coating, whereas the Mg content indicates an opposite trend (Fig. 2f).

Fig. 3 shows TEM micrographs and selected area electron diffraction (SAED) pattern of nano-Si and nano-Si/TiO2 specimens. The TEM images show that the Si particles are spherical in shape formed in the coatings with an average particle size of 30–40 nm (Fig. 3a). However after TiO2 coating, a thin film was formed on the Si surfaces. It was also observed that nano-sized TiO2 particles have smooth surfaces with spherical morphology and an average particle size of 70–80 nm (Fig. 3b). The SAED pattern of Si particle shows the polycrystallinity of the particles. The crystallinity of the TiO2 nanoparticle was verified using SAED pattern as shown in Fig. 3c. From the SAED pattern, the existence of ring corresponds to anatase and rutile structures of TiO2 which confirms the polycrystalline nature of the coating (Fig. 3d).

Fig. 4 shows the XRD patterns of the uncoated, Si and Si/TiO2 coatings deposited on the Mg–1 wt%Ca alloy. The peaks detected at 2θ values of 27.5°, 47.6°, 56.3° and 69.3° with orientation along (111), (200), (311) and (400) planes further confirmed the formation of Si film on the Mg alloy surface. Based on a comparison of the peak intensities, Si (111), a densely packed plane, is the preferred orientation in the silicon coating. However, Si/TiO2 coating presented peaks observed at 2θ values of 26.7° corresponding to the dominant peak of rutile TiO2(110), which has the highest peak intensity (relative to the other TiO2 planes). Besides, very weak diffraction peaks corresponding to the anatase (101), (004), of TiO2 (JCPDS 84-1286) are detected in the thinner TiO2 coating.

3.2. Immersion test

Fig. 5 shows the surface morphology of the uncoated, and Si and Si/TiO2 coated samples after being immersed in SBF for 168 h. It can be seen that the uncoated alloy is severely corroded with remarkable corrosion products and suffers from a large number of corrosion pits (Fig. 5a and d). Deep cracks also formed on the surface of the sample due to dehydration of the surface layer in air. The EDS analysis of the corrosion layer indicates that the presence of Mg and O as well as small amounts of P and Ca. The presence of high amounts of Mg and O indicated the formation of Mg(OH)2 (Fig. 5g). However the surface of Si coated sample composed of small amounts of corrosion products (Fig. 5b and e). The EDS analysis of the precipitate morphology indicates the presence of Mg, Ca, P, O and C elements which implied the formation of hydroxyapatite (HA) (Fig. 5h). The Si/TiO2 coated sample suffers from a much milder and more uniform corrosion attack compared to the uncoated sample (Fig. 5c and f). The attack by aggressive chloride ions in the SBF is responsible for the larger corrosion.
When specimens are immersed in the SBF, the MgO in the outer layer starts to react with the corrosive solution and converts to the insoluble Mg(OH)$_2$. However, the presence of aggressive Cl$^-$/CO$_2$ in the solution transformed Mg(OH)$_2$ into a more soluble MgCl$_2$ according to the following equations [14]:

$$\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2$$  \hspace{1cm} (1)

$$\text{Mg(OH)}_2 \rightarrow \text{Mg}^{2+} + 2\text{OH}^-$$  \hspace{1cm} (2)

$$\text{Mg}^{2+} + 2\text{Cl}^- \rightarrow \text{MgCl}_2$$  \hspace{1cm} (3)

Breakdown of Mg(OH)$_2$ decreases the protected area, consequently, promoting further dissolution of the substrate. Silicon oxide which forms as an inner layer is relatively more stable in the SBF compared to Mg(OH)$_2$ and MgO and can effectively resist chloride ions attack more effectively. Thus, the formation of the silicon-containing surface oxide layer provides a good barrier to enhance the corrosion resistance of the Mg–Ca alloy in chloride-containing solutions [1]. On the other hand, the presence...
of nano-TiO₂ particles as insoluble solid particles in the top layer would strengthen the barrier effect of the coating, which would further improve the corrosion resistance of the composite coating [15]. The EDS analysis of the corrosion products showed that it is composed of Mg and calcium phosphate (Fig. 5k). These corrosion products combined with Ti and Si films can further improve the corrosion resistance [2,3].

The degradation process of the bi-layered Si/TiO₂ composite coated Mg–Ca alloy is schematically illustrated in Fig. 6 and can be summarized as follows. The TiO₂ layer, as an outer first protection layer to the Mg–Ca alloy, contacts the solution first. Although the TiO₂ layer is uniform and homogeneously covers the Si layer, it is generally porous, and the solution can still reach the Si layer through the micro-pores and micro-flaws of the TiO₂ film (Fig. 6a). At this stage a corrosive electrolyte already occupied the porous outer layer, introduced new defects (big deep pores and cracks) and enlarged the existing ones, while the inner Si layer that contains pores as well is still intact. Further increase in immersion time causes the TiO₂ film to begin to degrade and experiences destruction, and Si film whose porosities are filled with the electrolyte becomes the second line of protection (Fig. 6b). However, this layer can protect the Mg–Ca alloy only for a certain duration owing to its small thickness and gradual dissociation in the electrolyte, thus more solution begins to interact with the Mg alloy directly. As the Mg–Ca alloy starts to degrade, Mg(OH)₂ starts forming at the coating interface with the alloy and HA starts forming on the outer surface providing further protection (Fig. 6c). At this stage the formation and enlargement of the defects slow down and accompanied with more Mg(OH)₂ and HA depositions (Fig. 6d). Eventually, some fragments of coating peel off from the substrate and corrosion products under the coating are exposed to the simulated body fluid. This explains the higher corrosion resistance achieved by the Si/TiO₂ coating.

The XRD pattern of the uncoated and coated samples immersed in SBF for 168 h show the existence of Mg(OH)₂ peaks accompanied by the peaks of Mg and HA (Fig. 7). The uncoated sample showed more broad Mg(OH)₂ peaks as main corrosion products than that of Si and Si/TiO₂ coated samples. The results of the X-ray further confirm the FTIR analysis indicating that the coated and uncoated specimens show a peak at 3704 cm⁻¹, corresponding to Mg(OH)₂ as the main corrosion product (Fig. 8). The existence of hydroxides in the corrosion products indicates a pitting type of corrosion attack [16]. Stable formation of Mg(OH)₂ is achieved by raising the pH value to about 11. However, augmentation of (OH)⁻ concentration leads to the development of Mg corrosion in localized regions [2] and results in hemolysis of cells. The C–O stretching of carbonate groups at 1473 cm⁻¹ and 883 cm⁻¹ is also observed, indicating the formation of hydroxyapatite. The precipitation of HA on the
surface of specimens can accelerate healing of the bone tissue indicating a good biocompatibility of the alloy. However, the P–O stretching of phosphate groups (1172 cm$^{-1}$ and 1090 cm$^{-1}$) was observed after immersion in SBF for 168 h. The broad absorption peaks at 3453 cm$^{-1}$ is related to the hydroxyl group and a weak band at 1657 cm$^{-1}$ is assigned to H$_2$O bending vibration.

The pH variation in the Kokubo solution with samples immersed for 168 h is shown in Fig. 9. It can be seen that the pH values of the Kokubo solution during the immersion of the coated samples are clearly lower than that of the uncoated sample over the time range. The pH value around implants is an important factor which can affect the cell differentiation, proliferation, and function. The alkalization can unfavorably affect the pH dependent physiological reaction balances in the vicinity of the Mg implant and may even lead to an alkaline poisoning effect [17]. It is obvious that the presence of TiO$_2$ as the top layer and Si as the inner layer caused a reduction in pH during immersion in the SBF and alleviate the local alkalization of the Mg–Ca alloy. For all the samples, the degradation of Mg(OH)$_2$ contributed most to the rapid increase in the initial pH due to the release of OH$^-$ ions [18]. However, the pH value became stabilized over longer immersion times. This may be due to the penetration of the solution into the interface between Si/TiO$_2$ coating and substrate via the pores and cracks of the coating when corroded by the SBF. The precipitation of apatite, which consumed OH$^-$ ions, could be another reason for the minimal pH increase at the final stage [19].

Fig. 7. X-ray diffraction patterns of uncoated Mg alloys, Si coated and Si/TiO$_2$ coated specimens after immersion in SBF solution for 168 h duration.

Fig. 8. FTIR absorption spectra of uncoated Mg alloys, Si coated and Si/TiO$_2$ coated specimens after immersion in SBF solution for 168 h duration.
The hydrogen evolution results of the uncoated, Si and Si/TiO$_2$ coated specimens in the Kokubo solution, for a period of 168 h, are shown in Fig. 10. The hydrogen evolution rates of the Si/TiO$_2$ and Si coated specimen are 1.57 ml/cm$^2$/day and 2.22 ml/cm$^2$/day, respectively. The value corresponding to Si/TiO$_2$ coated sample is significantly lower than the hydrogen desorption rate that could be tolerated by the human body (2.25 ml/cm$^2$/day) [20]. However, uncoated Mg–Ca alloys showed the highest hydrogen evolution rate (5.04 ml/cm$^2$/day). The rapid evolution of hydrogen bubbles result in significant subcutaneous gas pockets, which may delay the healing of surgical region, result in necrosis of tissues and cause discomfort [20]. In addition, generating high amount of gas from the biomaterial during the implant period leads to increment of pH, which results in hemolysis of cells [2]. The degradation rate of the Si/TiO$_2$ was much slower than that of the uncoated sample. The difficulty in charge transfer ascertains good corrosion protection ability for the Si and Si/TiO$_2$ coated samples [1]. The decline in degradation rate of Si/TiO$_2$ can be also explained by the accumulation of the corrosion products which formed a relatively more protective layer than that formed on the surface of the uncoated alloy, retarding the corrosion process.

3.3. Electrochemical measurement

Fig. 11 shows the cathodic and anodic polarization curves of the uncoated, nano-Si and nano-Si/TiO$_2$ composite coated specimens in the Kokubo solution. The corrosion potential ($E_{corr}$) of the uncoated Mg–Ca, nano-Si and nano-Si/TiO$_2$ coated specimens is $-1676$ mV$_{SCE}$, $-1601$ mV$_{SCE}$ and $-1539$ mV$_{SCE}$, respectively. The more positive corrosion potential of the Si/TiO$_2$ composite coated sample indicates that the corrosion reaction of the Mg–1 wt%Ca alloy is suppressed by the composite coating. The anodic polarization curves of the uncoated specimen shows a breakdown immediately after the initiation of polarization. The corrosion current density ($i_{corr}$) of the uncoated, Si and Si/TiO$_2$ coated specimens is 272.3, 39.7 and 25.2 $\mu$A/cm$^2$, respectively. The lower $i_{corr}$ values of Si and Si/TiO$_2$ coated samples indicate lower corrosion rates. This result indicates that the protectiveness of the Si/TiO$_2$ composite coating is higher than that of the Si coated sample. This is due to the presence of Si/TiO$_2$ films, which act as protective layers on the surface of the sample, causing a significant reduction in the corrosion rate. It was believed that the protective layer blocked the reaction allowing the transportation of species (such as water and chlorine), thereby increasing the corrosion resistance of the composite-coated samples as shown in Fig. 6. The corrosion current density ($i_{corr}$), corrosion potential ($E_{corr}$), cathodic Tafel slopes ($\beta_c$), anodic Tafel slopes ($\beta_a$) and the corresponding corrosion rate ($P_i$) of specimens extracted from the polarization curves are shown in Table 1. The corrosion rate ($P_i$) of samples obtained from the corrosion current density was measured according to the following equation [21]:

$$P_i = 22.85 \times i_{corr}$$  (4)

According to Eq. (1), Si/TiO$_2$ coating presented a lower corrosion rate (0.57 mm/year) compared to the Si coating.
However, the uncoated alloy indicated the highest corrosion rate (6.22 mm/year). The lower corrosion rate of the Si/TiO2 coating, compared to the Si coating, is due to the formation of a more uniform and compact protective film; which provides better protection for the Mg–1 wt%Ca alloy. The linear polarization resistance, \( R_p \), which is inversely proportional to the value of the corrosion current density, is calculated according to the following equation [22]:

\[
R_p = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c) i_{corr}}
\]

The polarization resistance of Si and Si/TiO2 coatings is 1.40 and 1.94 k\( \Omega \)cm\(^2\), respectively. These values are significantly higher than that of the uncoated alloy (0.36 k\( \Omega \)cm\(^2\)). It can be seen that the corrosion resistance of the Mg alloy was significantly improved after nano-Si/TiO2 composite coating due to the formation of dense barrier film on the substrate, which postponed penetrating of corrosive ions from the SBF solution. However, it is important to take into account that formation of a single Si film on the surface of the Mg–Ca substrate could not efficiently protect the specimen surface when exposed to physiological solutions due to surface morphology and structure of the Si film, which acts as a semi-mechanical barrier composed of some voids and micro-cracks. As a result, it could not adequately prevent the metallic ions transfer from the substrate. Therefore coating of nano-TiO2 as a top layer on the Si film can provide more protection of the substrate as the second layer (TiO2) reduces corrosion attacks and the inner layer (Si) protects the substrate from the corrosive medium when it passes through from the outer layer.

### 3.4. Mechanical properties

Table 2 shows the compression strength of the uncoated Mg–Ca, Si and Si/TiO2 coated specimens before and after immersion in SBF for 7 days. The compression strength of the uncoated Mg–Ca specimen before immersion was 224.2 MPa, while this value decreased 21% and reached to 176.5 MPa after immersion in the Kokubo solution (Fig. 12). The compression strength of the Si and Si/TiO2 coated specimens was 188.1 MPa and 198.3 MPa after immersion, respectively. These values are comparable to the compressive strength of human bones (100–230) MPa [23] in cortical bone. The after immersion strength of the mono-layered Si coated sample is 6% and of the Si/TiO2 composite coated sample is 11% higher than that of the uncoated Mg–Ca alloy. Therefore the Si/TiO2 composite coating can delay the loss of the mechanical property of the Mg–Ca alloy. Due to the higher density of the composite coating, it provided a better resistance to bio-corrosion and the compressive load of the samples with Si/TiO2 coating after immersion for 7 days is much higher than that of the uncoated sample. However, the mono-layered Si coated sample shows higher degradation rates compared to the Si/TiO2 composite coating because the mono-layered Si coating broke easily and the barrier property was lost resulting in the SBF reaching the substrates through the cracks and pores leading to loss of mechanical integrity. The Si/TiO2 composite coated sample demonstrated the highest compressive strength after immersion. This can be attributed to the compact and uniform structure with less pores and cracks in the coating.
Hence, the composite coating can effectively delay the decline in compressive strength of the Mg–Ca alloy, and provide sufficient support for the post-fracture bone healing.

4. Conclusions

The nano-Si and nano-Si/TiO₂ composite coatings were fabricated by the physical vapor deposition technique. The prepared nano-Si and nano-Si/TiO₂ films were uniform and compact composed of spherical particles with nano-size scale, However, there are some micro-pores and micro-cracks in both coatings to a different degree. The potentiodynamic polarization curves showed that corrosion potential shifted to the nobler direction and the current density decreased significantly for the nano-Si and nano-Si/TiO₂ composite coatings in reference to the uncoated Mg for the nano-Si and nano-Si/TiO₂ composite coatings in SBF. The compression tests showed that the nano-Si/TiO₂ composite coating can delay the loss of the compressive strength of the Mg–Ca alloy. The immersion test exhibited that the fine structure of the TiO₂ films induce more HA formation compared to both the Si-coated and the uncoated alloys in SBF indicating better biocompatibility.

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