ALKALI PRE-TREATMENT OF THE Ti6Al7Nb SUBSTRATE AND ITS IMPACT ON ELECTROCHEMICALLY DEPOSITED CALCIUM PHOSPHATE COATINGS

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Abstract

The aim of this work was to investigate the effect of alkali pre-treatment of a Ti6Al7Nb substrate on the morphology and physicochemical properties of calcium phosphate (CaP) coatings. CaP coatings were electrochemically deposited on two groups of substrates: one unmodified and the other pre-treated in a 5M NaOH solution. CaP coatings deposition was performed in a three-electrode system using a potentiostatic mode at a potential of -4 V for 1 h in an electrolyte containing 0.042M $Ca(NO_3)_2$ and 0.025M $NH_4H_2PO_4$. The surface characteristics of the coatings were determined using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), Raman spectroscopy, and contact angle techniques. Additionally, the corrosion resistance of the coatings was assessed by linear polarization resistance and potentiodynamic polarization tests in PBS solution. Morphological analysis showed that the coatings exhibited no significant differences. EDS analysis confirmed the presence of characteristic elements constituting the CaP coatings in both tested groups. Raman spectra revealed the characteristic peaks of the hydroxyapatite (HAp), amorphous calcium phosphate (ACP), and dicalcium phosphate dihydrate (DCPD) structures. Furthermore, Raman mapping confirmed the effectiveness of substrate pre-treatment, leading to the crystalline structure of the coatings. The water contact angle values indicated that pre-treatment of the substrate in NaOH increases the hydrophilicity of the deposited coatings. Regardless of the substrate preparation method, the deposited CaP coatings exhibited protective properties against corrosion under physiological conditions. The results confirmed that alkali pre-treatment of the Ti6Al7Nb alloy affects the crystallinity and the wettability of the electrodeposited CaP coatings.

Keywords: electrochemical deposition, hydroxyapatite coating, calcium phosphate, titanium alloys, Ti6Al7Nb, alkali surface modification

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Introduction

Currently, implants used in orthopaedics and dentistry are made of various materials, including metals such as titanium and its alloys, stainless steel or chromium-cobalt alloys [1]. These biomaterials have good mechanical properties and corrosion resistance, while being biotolerated and bioinert [2]. The key problem associated with their use is that they cannot form strong bonds with the bone after implantation. Due to the fact that the implant surface is the first to interact with tissues, surface modifications are used to enhance the biological response and osseointegration of the implant in the body [3]. By covering a metal implant with bioactive coatings, the mechanical properties of the substrate are preserved while also achieving the desired biological properties [4].

Calcium phosphate (CaP) coatings and, in particular, hydroxyapatite (HAp) coatings, seem to be an interesting solution due to their chemical similarity to hard tissues [5]. CaPs can serve as a scaffold for forming and regenerating bone tissue, and they are highly biocompatible, leading to stable implant osseointegration [6-8].

There are several techniques to apply CaP coatings to metallic substrates, including plasma spraying, dip coating, electrophoretic deposition, RF sputtering, sol-gel, and electrochemical deposition [7,9-11]. Many studies confirm the effectiveness of electrochemical deposition of CaP coatings and demonstrate the ability to control the chemical structure or morphology of the coating by selecting process parameters, electrolyte composition, electrolyte pH, or deposition temperature [9,12-16].

In order to obtain improved properties, such as better adhesion of the coating to the substrate, improved corrosion resistance and biological response, or more effective suppression of the release of toxic metal ions from the implant, the effect of using various pre-treatments before electrochemical deposition is investigated [17]. One way is to apply an alkali pre-treatment in a concentrated NaOH solution to a metal substrate [9,18]. Hydroxyl groups and the strong polar group of the produced sodium titanate may improve wettability [19]. De Oliveira et al. showed that cp-Ti grade 4 substrates, when pre-treated with 5M NaOH at 60°C for 24 h and subjected to heat treatment at 600°C and 900°C, exhibit complete hydrophilicity compared to the unmodified substrate [19]. The thin Na_2TiO_3 layer created on the surface of the titanium substrate facilitates improved calcium ions exchange and is a more desirable base for the deposition of hydroxyapatite than other CaPs [9,20]. Wettability is quite an important feature of implant surfaces, as it can significantly influence the cell-implant interaction. Many studies show that hydrophilic surfaces of biomaterials result in better growth of osteoblast cells [5,21,22]. Moreover, CaP coatings deposited on Ti-40Nb alloy and cp2-Ti substrates that were previously immersed in NaOH are characterized by greater roughness and a more developed morphology of the produced coating [23,24]. Corrosion resistance is crucial for biomaterials to uphold functionality, biocompatibility, and safety within the intricate biological environment of the human body [25]. Although titanium alloys are renowned for their corrosion resistance, surface treatments applied to them can significantly alter their corrosion behavior under physiological conditions.

Research on NaOH pre-treatment has been extensively conducted for the surface modification of pure titanium or Ti6Al4V alloy; however, there is limited literature on alkali pre-treatment without heat treatment of Ti6Al7Nb alloy prior to the electrochemical deposition process of CaP coatings. For that reason, this work presents research on the influence of NaOH solution pre-treatment of the Ti6Al7Nb substrate on the morphology, physicochemical properties, and corrosion resistance of the electrochemically deposited CaP coating.

Materials and Methods

Materials and pre-treatment

Disk samples from the Ti6Al7Nb alloy (Medgal Orthopaedic Implants and Instruments, Księżyno, Poland) with a diameter of 16 mm and a thickness of 6 mm were used as a substrate for the electrochemical deposition of calcium phosphate coatings. The substrates were processed using abrasive papers with grits ranging from 120 to 2500 and then polished with a colloidal silica suspension using an automatic polishing machine MECATECH 334 (Presi, France). The polished samples were first washed in an ultrasonic bath in ethanol and then rinsed with distilled water.
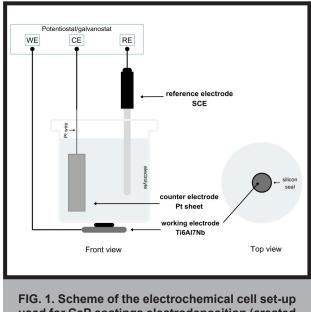
For further tests, the samples were divided into two groups: unmodified substrates and substrates prepared for immersion in NaOH prior to the electrochemical deposition process. The NaOH treatment consistent of soaking the samples in a 5M NaOH solution at 60°C for 24 h. Subsequently, the modified substrates were removed from the NaOH solution and washed with distilled water. Both groups were then subjected to electrochemical processes.

Electrochemical deposition of CaP coatings

CaP coatings were electrochemically deposited using a three-electrode system, where titanium alloy (unmodified and pre-treated in NaOH) was the working electrode (WE; with an exposed area of 0.79 cm^2), the platinum sheet was the counter electrode (CE), and the saturated calomel electrode (SCE, EUROSENSOR, Gliwice, Poland) was the reference electrode (RE) (FIG. 1). Electrolyte contained 0.042M Ca(NO$_3$)$_2$ (Chempur, Piekary Śląskie, Poland) and 0.025M NH$_4$H$_2$PO$_4$ (Chempur, Piekary Śląskie, Poland) and its pH was 4.60. The Ca/P molar ratio of 1.68 was similar to the stoichiometric hydroxyapatite (Ca/P 1.67). Electrochemical processes were carried out using the Autolab PGSTAT 302N potentiostat/galvanostat operated by NOVA 1.11 software (Metrohm, Autolab, The Netherlands). The CaP coatings were deposited potentiostatically at a potential value of -4 V vs. SCE for 1 h at 36°C. After the electrochemical deposition process was complete, the samples were rinsed with distilled water and dried in air at 36°C for 2 h (hereafter referred to as CaP-Ti6Al7Nb and CaP-NaOH-Ti6Al7Nb).

CaP coatings characterization methods

The surface morphology and local chemical composition of the CaP coatings were evaluated using a JEOL JSM-6610LV scanning electron microscope (SEM, JEOL, Tokyo, Japan), equipped with an energy dispersive X-ray spectroscopy (EDS) X-Max 80 microanalysis system (X-Max 80 EDS, Oxford Instruments, UK). Observations were made using magnifications of 100x, 250x, and 800x. EDS analysis was performed for three areas of the tested structures of the deposited CaP coatings on each of the samples in both groups.

FIG. 1. Scheme of the electrochemical cell set-up used for CaP coatings electrodeposition (created using canva.com [26]).

Raman spectroscopy studies were performed using an inVia Confocal micro-Raman spectrometer (Renishaw plc., Gloucestershire, UK) to determine the chemical structure. A laser beam with a wavelength of 532 nm and a 50x objective lens (Carl-Zeiss, Jena, Germany) was used, and analysis of the obtained Raman spectra was carried out in the range of 300-1500 cm^{-1}. Two-dimensional Raman maps were collected from 200x50 µm areas with 2 µm spatial resolution. All the collected Raman spectra and maps were pre-processed using WiRE 5.5 software.

Two samples from both groups were used for contact angle analysis. The water contact angles were analyzed using the drop shape analyser - DSA25 (KRÜSS GmbH, Hamburg, Germany). This examination was based on measurements using the sessile drop technique. The test liquid was deionized water, introduced in a volume of 0.8 µL, with three drops applied at different locations on the analyzed surface. Contact angles were measured after the surface reached equilibrium with the liquid in use.

Corrosion measurements were conducted in a PBS solution (phosphate buffered saline solution, pH 7.4, temp. 37°C, deaerated by bubbling with argon gas) using a potentiostat/galvanostat Autolab PGSTAT30 (EcoChimie, Utrecht, The Netherlands). A three-electrode measurement setup was used, with the tested samples (with an exposed area of 0.64 cm^2) serving as working electrodes, a platinum mesh as the counter electrode, and a saturated calomel electrode (SCE, EUROSENSOR, Gliwice, Poland) as the reference electrode. Before conducting the corrosion measurements, the samples were immersed in PBS solution under open circuit conditions for 1800 s to stabilize the open circuit potential (E_{OCP}). The linear polarization measurements were then performed within a scanning range of ±20 mV relative to the E_{OCP}, using a scan rate of 0.166 mV/s. Potentiodynamic polarization tests were carried out within the potential range from -0.4 V to +2 V with a scan rate of 1 mV/s. The results of the corrosion tests were analyzed using the CorrView software (Scribner Associates Inc.). Corrosion tests were repeated three times to ensure their reproducibility. The results are presented as mean values with standard deviations.

Results and Discussions

Morphology analysis

In FIG. 2, SEM images depict the surfaces of CaP coatings produced on both unmodified (FIGs 2a-c) and pre-treated (FIGs 2d-f) Ti6Al7Nb substrates. The CaP coating deposited on the unmodified titanium substrate exhibits a relatively dense and homogeneous structure (FIGs 2a-c). The presence of micropores can be observed (FIGs 2a-b), which may result from the release of hydrogen during electrochemical deposition (FIGs 2a-b) [9]. The CaP-NaOH-Ti6Al7Nb coating (FIGs 2d-f) also contains a small amount of micropores; however, these are sharper than those found in the CaP-Ti6Al7Nb coating (FIG. 2b). Higher magnification (FIGs 2e-f) also shows that the microcracks are not as extensive as those in the coating deposited on the unmodified substrate (FIGs 2b-c). The alkali treatment slightly changes the morphology of the deposited CaP coating. Additionally, it can be stated that the CaP coating on the substrate after alkaline treatment possesses a more compact structure (FIG. 2f).

Structural characterisation

The chemical structure of the modified samples was determined using Raman spectroscopy (FIG. 3a). The detailed analysis revealed that the obtained coatings consisted of a mixture of dicalcium phosphate dihydrate (DCPD), amorphous calcium phosphate (ACP), and crystalline hydroxyapatite (HAp), as shown in FIG. 3b. The formation of the DCPD phase is evidenced by the appearance of peaks at 986 and 1011 cm^{-1} in the Raman spectra, as illustrated in FIG. 3a. The v_1 mode is composed of a main contribution at 962 cm^{-1}, which is a typical peak of crystalline HAp, along with a weaker peak at 950 cm^{-1}, which is associated with the ACP phase [27-29].
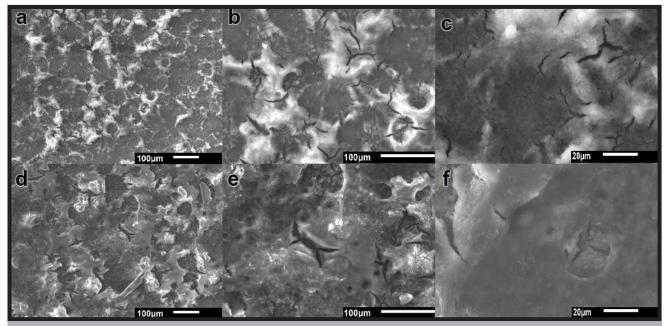

FIG. 2. SEM images of the surfaces: a-c) CaP-Ti6Al7Nb, d-f) CaP-NaOH-Ti6Al7Nb.
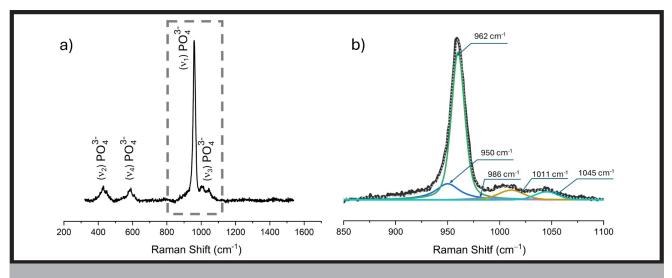

FIG. 3. Example of Raman spectra analysis of an electrochemically deposited CaP coating on an unmodified substrate (the dotted line represents the sum of the single peaks used for fitting).

Raman mapping analysis was carried out to determine the structure of CaPs in the Raman shift range of 800-1100 cm^{-1}. By calculating the ratio of the peak area at approximately 950 cm^{-1} to the peak area at approximately 962 cm^{-1} (I_{950}/I_{962}), it is possible to find ACP (or HAp)-rich areas and ACP (or HAp)-poor areas. FIG. 4a and FIG. 4b show the I_{950}/I_{962} ratio of Raman mapping of the CaP coatings deposited on the unmodified substrate and pre-treated substrate, with the examined area size of 200x50 μm^2.

The images indicated that pre-treatment of titanium alloy substrates in a 5M NaOH solution leads to the formation of CaP coatings with a higher content of the HAp crystalline phase, as evidenced by the predominance of the dark color that reflects a low presence of amorphous calcium phosphate forms. Nevertheless, even in these samples, micro-areas were found where the amount of amorphous phase was higher. It can be concluded that the CaP coatings produced using the developed technology, whether or not the alkali pre-treatment is applied, are not homogeneous in terms of chemical structure.
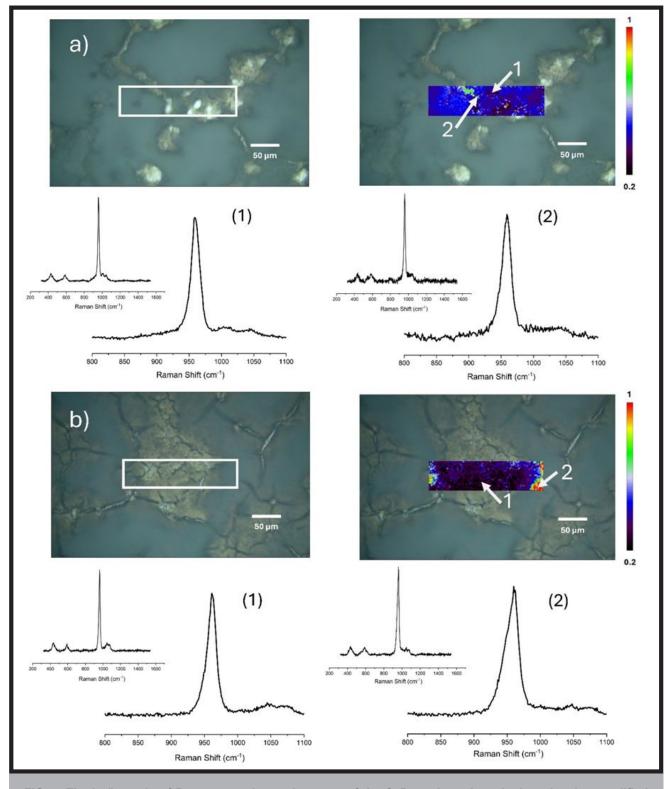

FIG. 4. The I_{950}/I_{962} ratio of Raman mapping and spectra of the CaP coatings deposited on the a) unmodified Ti6Al7Nb substrate, b) modified Ti6Al7Nb substrate.

Example EDS spectra of the point chemical composition analysis for selected areas of CaP coatings deposited on both the unmodified and the pre-treated substrates are presented in FIG. 5. The EDS analysis confirmed the presence of Ca, P, and O elements in the CaP coatings as well as the substrate elements: Ti, Al, and Nb. The molar ratio of Ca/P in stoichiometric hydroxyapatite is 1.67 [30]. The obtained results of Ca/P ratio have very similar values to stoichiometric hydroxyapatite, which indicates its presence on the substrate (1.68 and 1.54 for CaP-Ti6Al7Nb and CaP-NaOH-Ti6Al7Nb, respectively).

Analyzing the EDS results, it can be concluded that a value closer to the stoichiometric ratio was obtained for the coating deposited on the unmodified substrate (Ca/P≈1.68). Conversely, the Ca/P ratio of the coating deposited on the pre-treated substrate is slightly lower than the desired value, suggesting a calcium deficiency in the examined areas of both coatings. Thus, the Ca/P ratio corresponds to calcium deficient hydroxyapatite (CDHAp) [7]. Furthermore, the presence of titanium and other alloy components may result from an irregular coating of the substrate or a relatively thin coating.
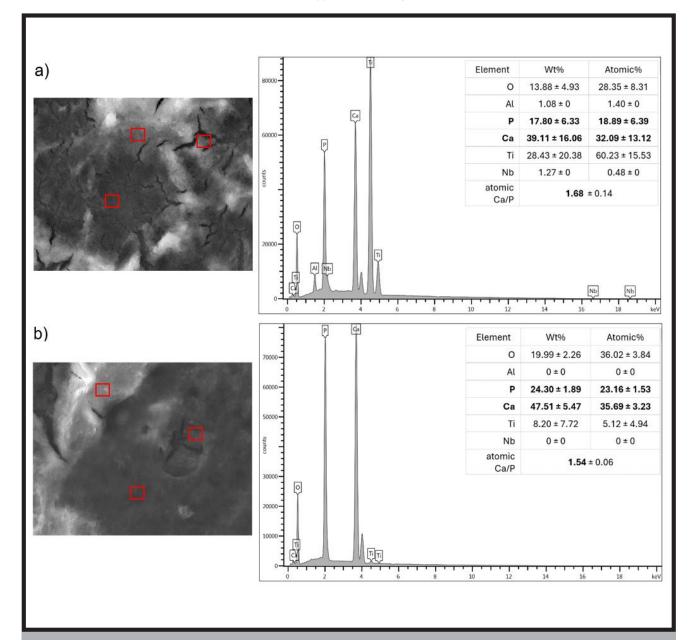

FIG. 5. Example EDS spectra and elemental composition analysis of: a) CaP-Ti6Al7Nb, b) CaP-NaOH-Ti6Al7Nb (inset with squares shows the analyzed areas).

Corrosion characteristics

The evaluation of a material's susceptibility to corrosion can rely on several corrosion parameters, including open circuit potential E_{OCP}, polarization resistance R_p, corrosion current density I_{cor}, and potentiodynamic characteristics. In this study, E_{OCP} was taken as the potential of the sample that stabilized under open circuit conditions within 1800 seconds. R_p and I_{cor} were determined from the linear polarization measurements using the CorrView software. R_p was calculated as the inverse of the slope of the I vs. E curve near the E_{OCP}, whereas I_{cor} was calculated based on the Stern-Geary relationship using the Stern-Geary Coefficient of 26 mV. FIGs 6a-b present values of E_{OCP}, R_p and I_{cor} determined for polished Ti6Al7Nb alloy, Ti6Al7Nb alloy pre-treated in NaOH, and CaP-coated alloy substrates (without and after treatment in NaOH) in PBS solution. A shift to more noble values of E_{OCP} can be observed for the CaP-Ti6Al7Nb and CaP-NaOH-Ti6Al7Nb samples, although surface pre-treatment in NaOH results in slightly lower E_{OCP} values (FIG. 6a). Both the CaP-Ti6Al7Nb and CaP-NaOH-Ti6Al7Nb samples exhibit higher R_p and lower I_{cor} values (FIG. 6b), indicating the barrier nature of electrodeposited CaP coatings. Such barrier coatings limit the transition of ions and electrons between the substrate and the electrolyte, reducing the corrosion rate [31]. However, the most significant changes in R_p and I_{cor} (approximately 70 times compared to the bare alloy) and thus the best corrosion protection, are observed for the CaP-Ti6Al7Nb.

The shape of the potentiodynamic curves presented in FIG. 6c is typical for titanium and titanium-based alloys reflecting their high passivity in physiological solutions [32]. None of the investigated samples display an active region because of the passive oxide layer formed on their surfaces. Notably, the positive effect of pre-treatment in NaOH is evident, as the corrosion current density in the Tafel range is much lower compared to the unmodified alloy. Furthermore, for the NaOH-treated Ti6Al7Nb alloy, the passive current density has a lower value when compared to the unmodified sample, indicating a much more effective surface passivation in the alkaline solution. The potentiodynamic characteristics received for CaP-Ti6Al7Nb and CaP-NaOH-Ti6Al7Nb samples confirm the previously suggested barrier nature of electrochemically deposited CaP coatings. As can be seen from FIG. 6c, the electrodeposition of the CaP resulted in a lower corrosion current density, indicating improved stability and corrosion resistance, especially for the CaP-Ti6Al7Nb sample, for which the corrosion potential is also shifted towards more positive values. The passivity of the tested samples is evidenced by a wide current density plateau with low passive current densities (approximately 10^{-6} A/cm^2) observed during further polarization. For the CaP-coated samples, the passive region is narrower than that of the unmodified and NaOH-treated Ti6Al7Nb alloy, with transpassivation occurring at 1.6V vs. SCE. No signs of pitting corrosion (anodic breakdown) were observed for any of the samples within the studied potential range (up to 2V vs. SCE), as indicated by the absence of a hysteresis loop on the reverse scan, meaning that the samples maintain their passivity without forming pits.
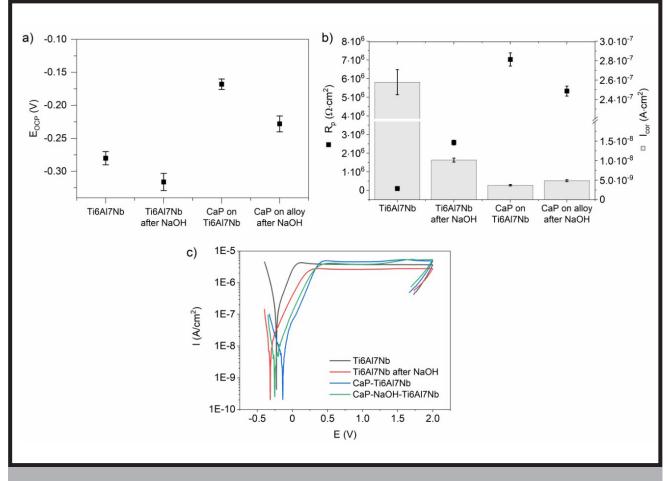

FIG. 6. Corrosion characteristics of Ti6Al7Nb alloy without and with CaP coatings in PBS solution: a) open circuit potential E_{OCP}, b) polarization resistance R_p and corrosion current density I_{cor}, c) potentiodynamic polarization curves.
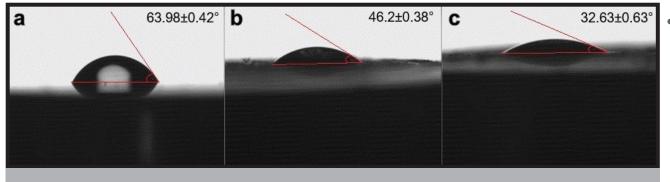
FIG. 7. Water drops on different surfaces: a) unmodified Ti6Al7Nb, b) CaP-Ti6Al7Nb, c) CaP-NaOH-Ti6Al7Nb.

Wettability studies

Among all the tested samples, the surface of the unmodified titanium alloy is characterized by the highest water contact angle value, which is 63.98±0.42° (FIG. 7a). However, electrodeposited CaP coatings further enhance the surface's hydrophilic nature, especially when the substrate was pre-treated with NaOH solution. The contact angle of the CaP-Ti6Al7Nb surface is 46.2±0.38° (FIG. 7b), and that of CaP-NaOH-Ti6Al7Nb is 32.63±0.63° (FIG. 7c), indicating that the surface with the coating deposited on the modified substrate has improved hydrophilicity. In the case of the NaOH-treated substrate, it was impossible to determine the contact angle, as water spread completely across the surface. Therefore, it can be concluded that the Ti6Al7Nb alloy surface after NaOH treatment is fully hydrophilic, showing complete wetting by water with a contact angle of 0°. The higher hydrophilicity of titanium-based substrates treated with NaOH solution has already been reported in the literature [4,33]. This phenomenon is attributed to the formation of a Na_2TiO_3 layer on the surface, enriched with highly polar hydroxyl groups that enhance surface wettability [34]. According to literature reports, hydrophilic surfaces with a contact angle in the range of 20-40° promote better cell proliferation, suggesting that CaP coatings electrodeposited on the surface of the NaOH-treated Ti6Al4V alloy will facilitate favorable cell-surface interactions [33,35,36].

Conclusions

Unmodified and pre-modified Ti6Al7Nb samples were used as substrates for the electrochemical deposition of CaP coatings. The main objective of this study was to investigate the influence of alkali pre-treatment of the substrates on the surface morphology, physicochemical properties, and corrosion resistance of the electrochemically deposited CaP coatings.

SEM, EDS, and Raman spectroscopy confirmed the successful deposition of CaP coatings on both substrates. SEM analysis did not reveal any significant differences in the morphology of the deposited CaP coatings. EDS analysis showed that the Ca/P atomic ratios of both coatings are similar to the stoichiometric hydroxyapatite. The electrodeposited CaP coating acts as a protective barrier for the titanium alloy substrate, thereby enhancing its corrosion resistance in physiological solutions, as confirmed by the corrosion tests.

The presented results indicated that the alkali pre-treatment of the substrate affects the physicochemical properties of the CaP coatings, increasing their crystallinity and surface hydrophilicity. These findings provide valuable insights for future research into bone cell interactions.

Acknowledgements

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