

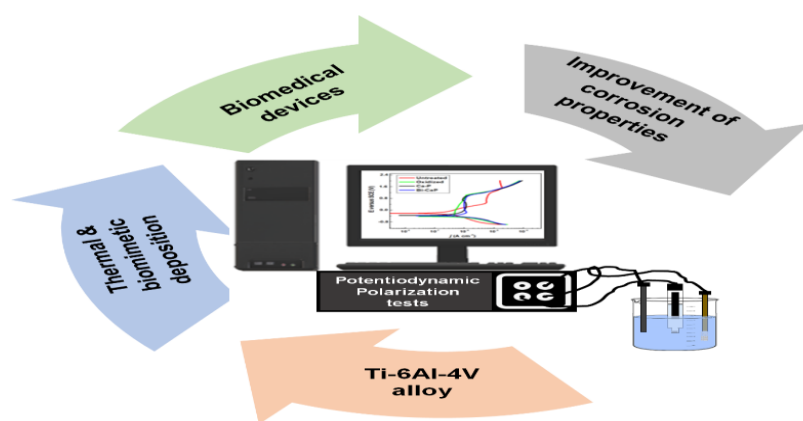
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New Findings Regarding the Thermal Oxidation and Biomimetic Depositions on the Corrosion Resistance of the Ti-6Al-4V Alloy

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Our research group has been working on the surface functionalization of Ti-6Al-4V alloy by using thermal oxidation followed by CaP and Bi-CaP biomimetic depositions. In this short communication, we present new insights into the corrosion behaviour of the treated system by using potentiodynamic polarization tests. Our results demonstrated lower values of electric current density for the CaP specimens when compared to the Bi-CaP, indicating a tendency for the CaP samples to remake the passive film. Another reasonable explanation may be related to the displacement of CaP particles or the formation of corrosion products that partially block the pores of the coating. Morphological analyzes of all treated surfaces after the potentiodynamic polarization tests also suggest the improvement of the corrosion resistance of the Ti-6Al-4V alloy.

Graphical abstract



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1. Introduction

As mentioned by Gautam et al [1], biomedical implants demand has increased recently due to poor lifestyles as well as the age structure of the world population. In general, implant failure reasons include infections, fractures, septic inflammations, and corrosion processes [2]. Titanium alloys

have been widely used in several sectors owing to its excellent properties, such as high specific strength, low density, and good biocompatibility [3, 4]. However, one of the main disadvantages observed in the use of titanium alloy implants is the premature failure due to the localised and global

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corrosion processes [5].

In other words, the TiO_2 coating that forms spontaneously on the titanium alloys surface is not able to protect the material from the corrosive process in certain environments. In this sense, surface treatments become necessary to improve the corrosive properties of the material. Recent studies have shown [6] the thermal oxidation treatment improved the surface mechanical properties as well as the corrosion responses of the Ti-6Al-4V alloy widely used as biomaterial. The results obtained by using electrochemical impedance spectroscopy (EIS), demonstrated that the thermal oxidized Ti-6Al-4V alloy containing Bi-CaP as well as CaP, presented greater corrosion resistance when compared to the bare material after 24 h of immersion time in Hank's solution.

Here, we display new insights into the corrosion behaviour of a double film formed on the Ti-6Al-4V alloy surface by using thermal oxidation and biomimetic deposition containing CaP and Bi-CaP via potentiodynamic polarization tests.

2. Material and Methods

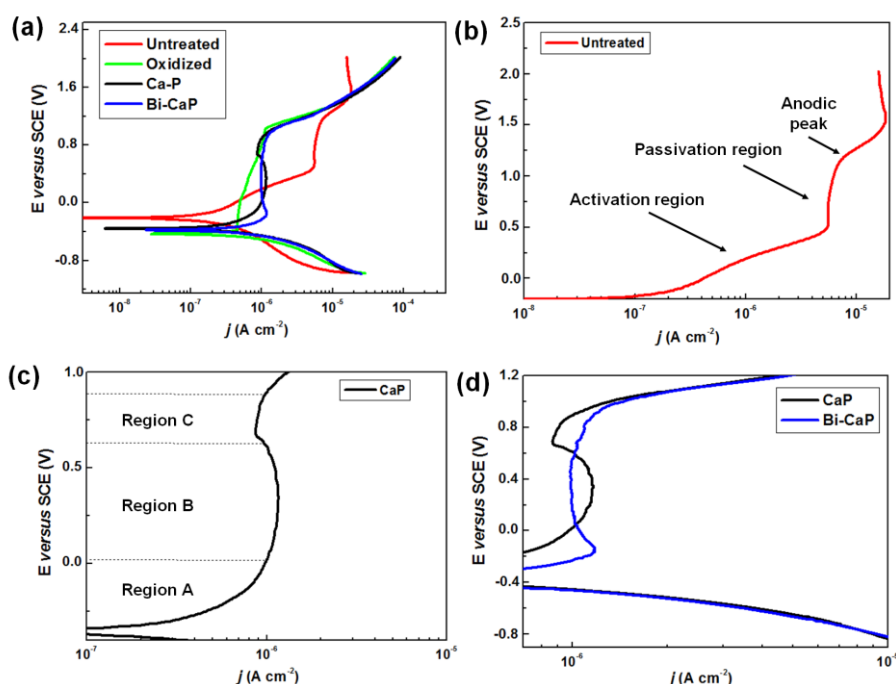


Figure 1. (a) Potentiodynamic polarization curves for Ti-6Al-4V alloy, oxidized Ti-6Al-4V alloy as well as Ti-6Al-4V after thermal oxidation and biomimetic deposition of CaP and Bi-CaP, (b) details of the anodic branch of the untreated alloy, showing the activation region, passivation region and anodic peak, (c) details of the distinct three regions (A, B and C) for the CaP specimen, (d) Comparison of CaP and Bi-CaP conditions in the potential range of -0.44 to $1.03 V_{SCE}$.

3. Results and Discussion

Potentiodynamic polarization curves (see **Figure 1 (a)**) were obtained for, at least, three samples of Ti-6Al-4V alloy, oxidized Ti-6Al-4V alloy, Ti-6Al-4V after thermal oxidation and biomimetic deposition of CaP and Bi-CaP. As can be seen, the untreated sample presented a corrosion potential ($E_{i=0}$) slightly more positive ($E_{corr} = -0.19 V_{SCE}$) when compared to the treated specimens ($E_{corr} = -0.44 V_{SCE}$ (oxidized), $E_{corr} = -0.36 V_{SCE}$ (CaP) and $E_{corr} = -0.37 V_{SCE}$ (Bi-CaP)). For a passive alloy as Ti-6Al-4V, it is almost impossible to determine the

Details regarding the Ti-6Al-4V alloy used in the present work, the oxidation treatment and the biomimetic of CaP and Bi-CaP deposition can be found in reference [6]. The corrosion potentials (E_{corr}) of the studied samples were monitored during 3600 s and are not shown here. Potentiodynamic polarization measurements were carried out in the range -0.90 to $2.00 V_{SCE}$ with a potential scan rate of 0.5 mV s^{-1} , using a modular AUTOLAB Multi Potentiostat model PGSTAT128N in Hank's solution (NaCl : 8.0, KCl : 0.40, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$: 0.06, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$: 0.10, CaCl_2 : 0.14, $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$: 0.06, NaH_2PO_4 : 0.06, Glucose: 1.00, NaHCO_3 : 0.35, g L^{-1} , respectively) at 37 ± 1 °C. A classical three-electrode configuration electrochemical cell was used: the functionalized samples as working electrode, a saturated calomel reference electrode, $\text{Hg}/\text{Hg}_2\text{Cl}_2$, KCl_{sat} , and a platinum auxiliary electrode. The geometric area used on the potentiodynamic polarization tests were 0.78 cm^2 for untreated, 0.68 cm^2 for oxidized, 0.67 cm^2 for CaP, and 0.79 cm^2 for Bi-CaP. The morphology of the functionalized surfaces was obtained by SEM technique before and after the corrosion tests. For this purpose, a scanning electron microscopy (SEM) (Hitachi-TM3000) with energy dispersive X-ray spectroscopy SEM/EDS was used.

anodic Tafel slope, due to the passive region where a constant current density is present. So, it can be concluded the corrosion current density (i_{corr}) is limited by the cathodic branch, presenting a very similar values for all specimens.

In fact, there are no significant changes in the cathodic branch since there is practically a reduction in dissolved oxygen. In this way, the increase of anodic reaction shifted the corrosion potential to more negative values. As shown on the potentiodynamic polarization curves (see **Figure 1 (b)**), after the corrosion potential, there is an activation zone for the untreated material with subsequent passivation in a potential range of 0.5 to $1.2 V_{SCE}$, exhibiting an increase of the electric current density ($\sim 2.0 \times 10^{-6} \text{ A/cm}^2$). An anodic peak around 1.3

V_{SCE} was observed for the untreated material, which corresponds to the accentuation of the TiO_2 oxidation process according to the Pourbaix diagram [7]. The thermal oxidation and biomimetic deposition of CaP and Bi-CaP reduced the passivation current density (i_p) to smaller values for all specimens.

With respect to CaP material (see **Figure 1 (c)**), three distinct regions could be identified (Regions A, B and C). Region A presents an electric current density of the order of 10^{-7} A/cm² over a potential range of 0.33 to 0.026 V_{SCE} . An increase in the electric current density ($\sim 1.01 \times 10^{-6}$ A/cm²) was verified until reaching the potential of 0.60 V_{SCE} (region B). An opposite effect (decreasing of the electric current density) was measured in the potential range from 0.61 to 0.87 V_{SCE} . Furthermore, lower values of electric current density were observed for the CaP conditions when compared to the Bi-CaP (see **Figure 1 (d)**). These findings indicate a tendency for the functionalized material to remake the passive film. Another reasonable explanation may be related to the

displacement of CaP particles or the formation of corrosion products that partially block the pores of the coating.

Morphological analyzes of all treated surfaces after the potentiodynamic polarization tests are displayed in **Figure 2**. The morphology of the Ti-6Al-4V alloy after the oxidized treatment may be verified in **Figure 2 (a)**. It should be noted that there were risks on the alloy surface as well as localized corrosion regions. Here, the scratches are due to the mechanical polishing process. Regarding to the CaP treatment (see **Figure 2 (b)**), it is possible to verify a less intense localized corrosion process, demonstrating the effect of surface treatment. **Figure 2 (c)** illustrates the SEM image related to the Bi-CaP condition. It can also be suggested that the thermal oxidation followed by Bi-CaP biomimetic deposition improved the corrosion properties of the Ti-6Al-4V alloy. The potentiodynamic polarization results are supported by previously published EIS results [6]. Furthermore, typical structures of hydroxyapatite can be seen in **Figure 2 (c)**.

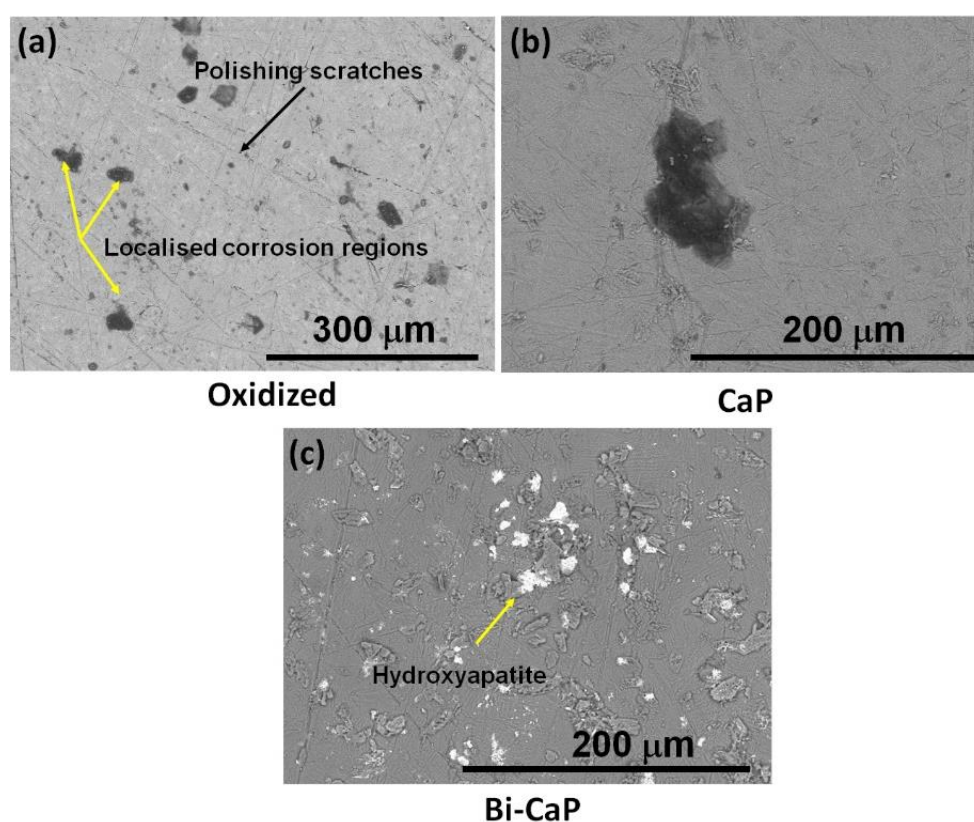


Figure 2. SEM images of the Ti-6Al-4V titanium alloy after thermal oxidation and biomimetic deposition of (a) oxidized, (b) CaP, and (c) Bi-CaP. Magnification of 350 x (oxidized sample) and 500x (CaP and Bi-CaP).

4. Conclusions

The corrosion behaviour of the Ti-6Al-4V alloy coated with a double layer composed of rutile and Bi-doped CaP was verified in the present survey via potentiodynamic polarization tests. The results obtained in the present work demonstrated lower values of electric current density for the CaP specimens when compared to the Bi-CaP, indicating a tendency for the CaP samples to remake the passive film. Another reasonable explanation may be related to the displacement of CaP particles or the formation of corrosion products that partially block the pores of the coating. Furthermore, morphological results helped us to address the global corrosion process.

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Author Contributions

Carolina Aurélia Ribeiro Maestro: Conceptualization, Methodology, Validation, Formal analysis & Investigation. Alysson Helton Santo Bueno: Formal Analysis. Roseli Marins Balestra: Formal Analysis. Artur Mariano de Sousa Malafaia: Formal Analysis. Jéferson Aparecido Moreto: Writing – original draft, Writing – review & editing.

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