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Calcium Phosphate Formation on Alkali-Treated Titanium Alloy and Stainless Steel

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Alternatives to the plasma spraying method have been developed to obtain calcium phosphate coatings, like the biomimetic method. This process is a physicochemical method in which a substrate is soaked in a solution that simulates the physiological conditions, for a period of time enough to form a desirable layer of the calcium phosphate on the substrate. The titanium substrate usually investigated in the literature is subjected to an alkali treatment to induce the calcium phosphate formation and improve adhesion of the coating. The goals of this work are to compare the effect of alkaline treatments on two substrates titanium alloy and stainless steel, usually used for implants and orthopedic prostheses. The metallic substrates were treated with NaOH 5N at 60 °C for 24 h and NaOH 20N at 90 °C for 30 min. The samples were immersed in simulated body fluid for 3 days and in a solution with a higher calcium concentration for another three days. The modified substrates and coatings were characterized using profilometry, scanning electron microscopy and X-ray diffraction analysis. The alkaline treatment modified the characteristics of both substrates and allowed the nucleation a calcium phosphate film.

Keywords: *Titanium alloy, stainless steel, alkali treatment, calcium phosphate coatings, biomimetic*

1. Introduction

One of the areas of Materials Engineering of large potential and impact in the improvement of human and animal quality of life is Biomaterials, especially Bioactive Ceramics. Bioactive ceramics, however, present low toughness, which limits their use “in vivo”. An alternative for the low toughness is coating metallic substrates with good acceptance “in vivo”, such as titanium, with bioceramics. Several physical and chemical methods have been employed to obtain coatings using bioactive ceramics depending on each specific substrate. Among these methods the Plasma Spraying is the most investigated. Alternatives to the Plasma Spraying method have been developed to obtain films of calcium phosphate, like the Biomimetic Method[1-4]. The biomimetic process is a physicochemical method in which a substrate is soaked in a solution that simulates the physiologic conditions, for a period of time enough to form a desirable layer of calcium phosphate on the substrate. Previously to the immersion in the simulated body fluid solution, the substrate is usually treated with an alkaline solution to generate a modified surface that induces the calcium phosphate layer formation. In the case of the titanium substrate a titanate hydrogel $HTiO_3^+$ forms upon NaOH treatment. A subsequent heat treatment dehydrates this hydrogel layer and stabilizes it by the formation of an amorphous sodium titanate layer ($HTiO_3Na$)[5,6]. Advantages of this method are its simplicity and its low investment cost in relation to the plasma spray process usually used. Besides, it can be used to coat substrates with complex geometry or porous substrates, and it makes it possible to include organic molecules in the film to induce and to accelerate the regeneration of living tissues[2].

Although biomimetic calcium phosphate coatings have been largely studied on titanium substrate there are no corresponding studies concerning the development of biomimetic coatings on stainless steel substrate. This is also an important metallic alloy used for orthopedic implants,

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specially in Brazil. The goal of the present work is therefore to obtain biomimetic calcium phosphate coatings on stainless steel AISI 316L substrates and on titanium alloy ASTM F136. Two alkaline treatments (NaOH 5 N and NaOH 20 N) were used and the coatings were produced by immersion in simulated body fluid solutions (SBF). The modified substrates and the obtained coatings were than characterized by several techniques.

2. Materials and Methods

Titanium alloy Ti6AL4V ASTM F136 (Ti) and stainless steel AISI 316L (SS) plates were cut into small rectangular samples (20 mm, 10 mm, 1 mm). The plates were metallographically gritted until 1000# using a SiC emery paper and ultrasonically cleaned in water and acetone. The plates were divided into two groups. The first group was soaked in 5N NaOH solution at 60 °C for 24 h, following a procedure used for biomimetic coatings on titanium[6]. The second group was soaked in 20N NaOH solution at 90 °C, 30 min. This treatment was intended to give isocorrosion conditions for the two alloys studied[7,8]. The treated samples were ultrasonically washed three times in deionized water for 10 min. Both specimens were dried at 40 °C for 24 h. They were subsequently heat-treated for 3 h in air atmosphere, at 600 °C in the case of Ti and 900 °C in the case of SS.

A calcium phosphate coating was produced on substrates by immersion in a solution that simulates the inorganic part

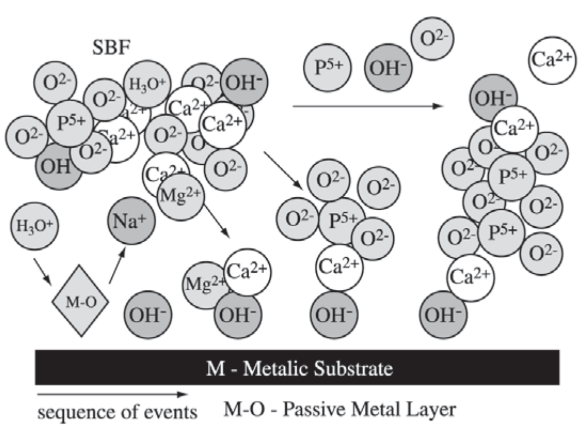

Figure 1. Schematic representation of calcium phosphate nucleation on the surface of alkali treated metal soaked in SBF.

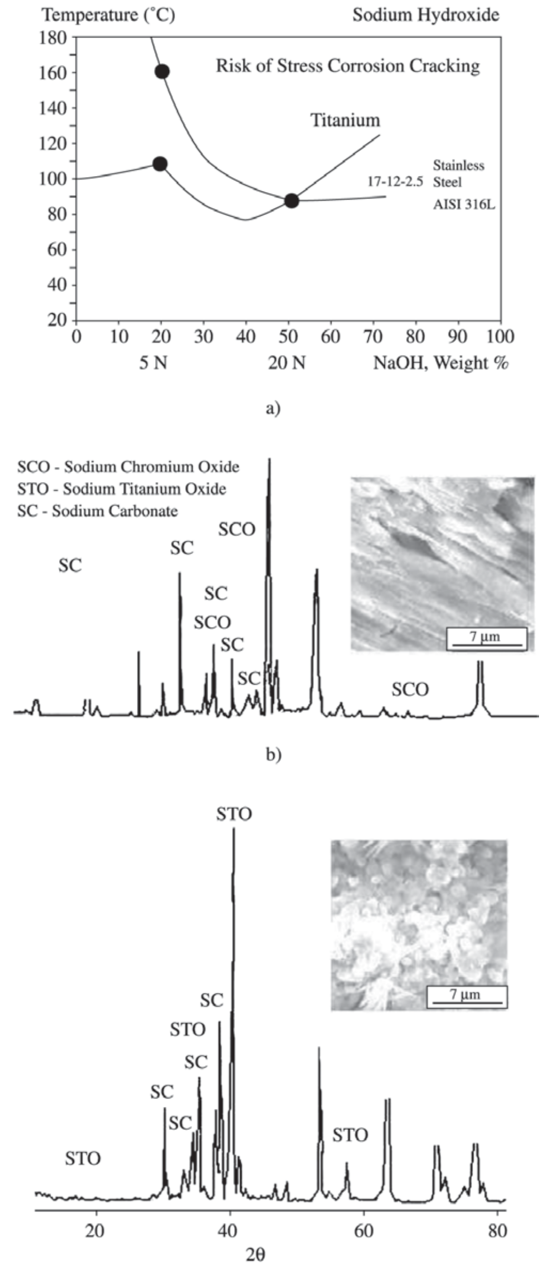

Figure 2. a) Isocorrosion Diagram in NaOH; b) XRD and SEM microphotography of SS treated in NaOH 20N; c) XRD and SEM microphotography of Ti treated in NaOH 20N, and gently rinsed in water. Peaks not identified correspond to the substrates Ti and SS.

Table 1. Ion Concentration of Human Blood Plasma and SBF.

Ions	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}
SBF (mM)	142.0	5.0	1.5	2.5	147.8	4.2	1.0	0.5
Blood Plasma (mM)	142.0	5.0	1.5	2.5	103.0	27.0	1.0	0.5

of human blood plasma (SBF). Its composition is given in Table 1 and is compared with that of human blood plasma. The solution was prepared by dissolving reagent-grade NaCl, KCl, $NaHCO_3$, $MgCl_2 .6H_2O$, $CaCl_2$ and KH_2PO_4 into distilled water and buffered at pH=7.25 with TRIS (tris-hydroxymethyl aminomethane) and HCl 1N at 37 °C [9]. The samples were soaked at 37 °C for 3 days and then in a solution 1,5SBF (a solution with Ca^{2+} concentration 1,5 higher) for 3 days.

The effects of alkaline treatment on the surface of the substrate and the structure of the coatings obtained were evaluated using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDAX) and X-ray diffraction analysis (XRD). The surface texture evaluation was accomplished by stylus profilometry (HommelWeeke Lv100 and Hommel Tester T8000). The measurement was done by the movement of the probe always perpendicular to the original direction of waves produced by previous grinding of the samples.

3. Results and Discussion

Generally, the surface of the metallic substrate is covered with a thin passive layer (Fig. 1). During alkaline etching, this Metal-O passive layer dissolves to form Metal-OH. The amorphous Metal-OH layer formed on the surface induces the calcium phosphate nucleation. Upon exposure to SBF, the thus treated substrates adsorb Ca^{2+} and Mg^{2+} ions from SBF via ion exchange. The adsorbed Ca^{2+} and Mg^{2+} ions accelerate the calcium phosphate nucleation by increasing the ionic activity of phosphates forming[10,11]. Thus a good Metal-OH layer is vital to the nucleation of a calcium phosphate layer (CPL).

Biomimetic coatings on Titanium substrate studies reported in the literature usually use a substrate treatment with NaOH 5N solution[5,6]. In this work, besides this condition another treatment was performed based on the knowledge of the isocorrosion diagrams for Ti and SS[8] shown in Fig. 2a.

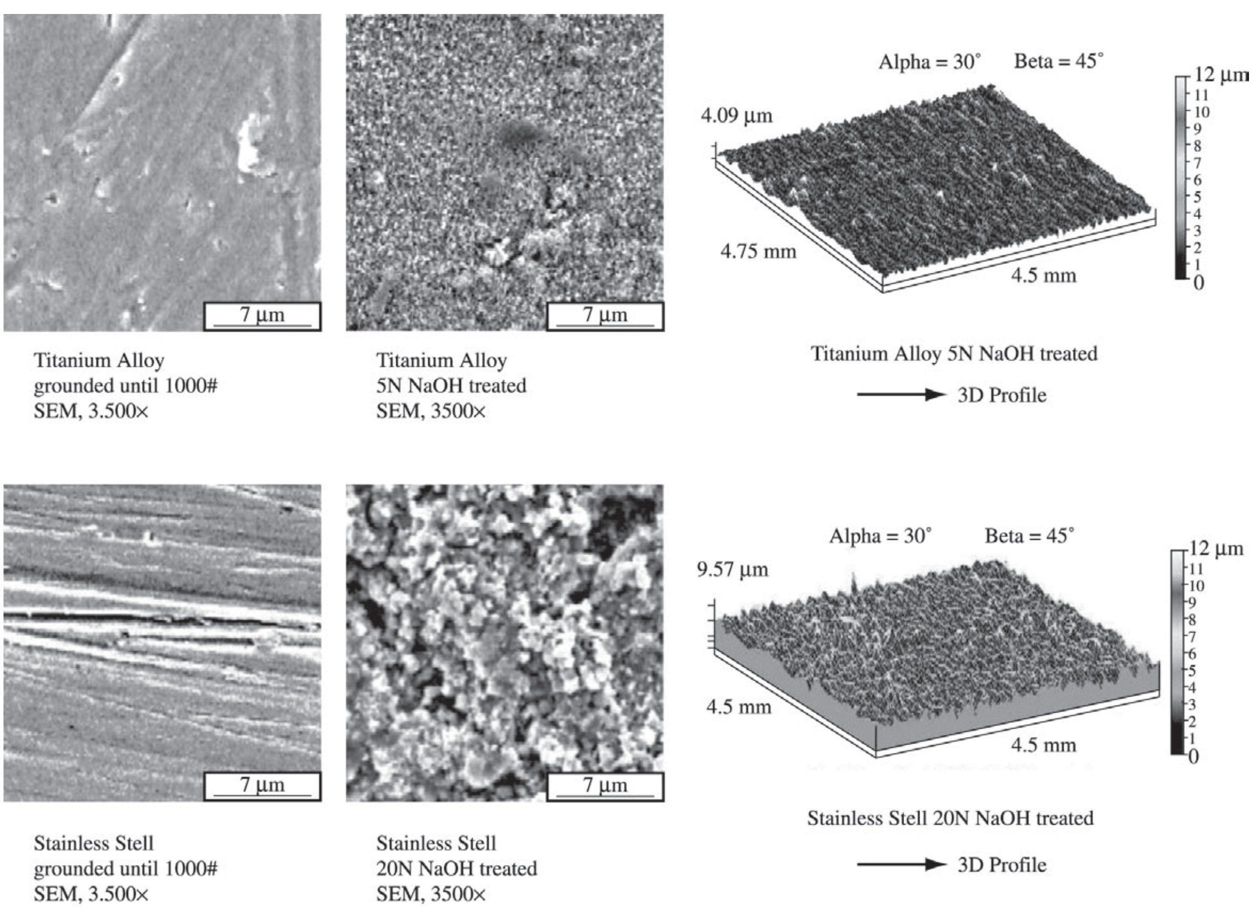

Figure 3. SEM images and 3D profiles of a) stainless steel treated in NaOH 20N and b) titanium alloy treated in NaOH 5N.

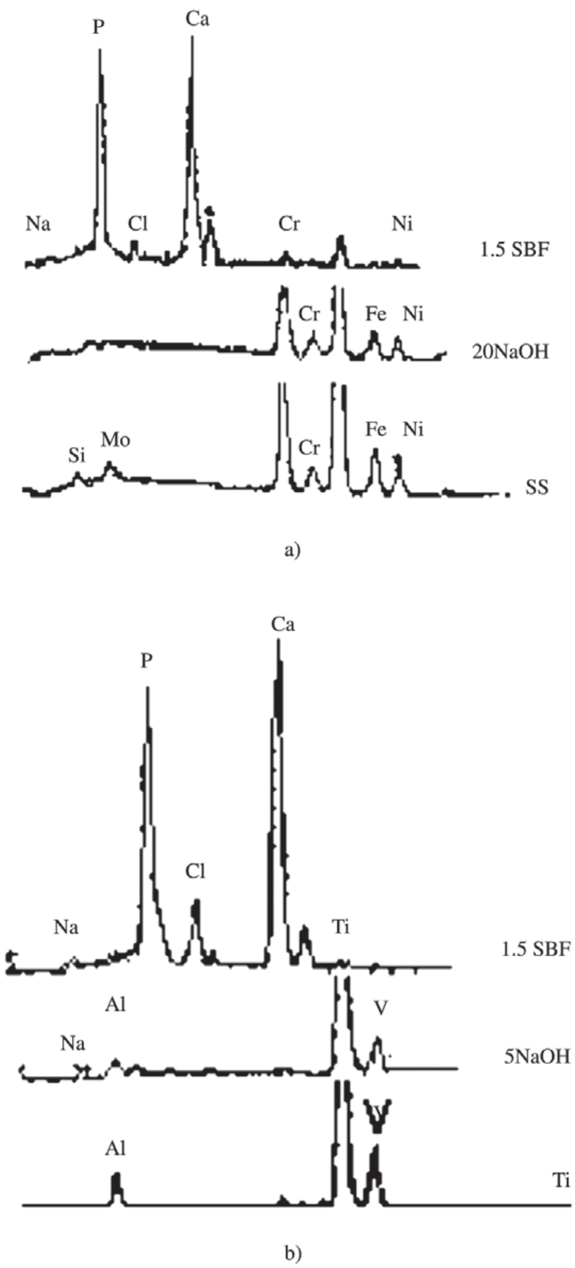

Figure 4. EDAX patterns of a) stainless steel treated in NaOH 20N and soaked in 1.5SBF; b) titanium alloy treated in NaOH 5N and soaked in 1.5SBF.

A comparative point for surface attack of the two substrates was determined as NaOH 20N solution at 90 °C. After the alkali treatment and just a gentle washing by immersion in water, the XRD patterns of the substrates indicated the presence of sodium titanium oxide on Ti and sodium chromium oxide on SS (Fig. 2a and 2c). It was also observed the presence of an undesirable layer of sodium carbonate, especially on the 20N treated samples. Such sodium carbonate layer was removed by ultrasonically washing the samples, according to the procedure described in the methodology.

Besides the creation of a hydrated oxide layer, necessary for the CPL nucleation, the chemical attack also leads to a modification in the texture. Figure 3 illustrates SEM images and 3D profiles of NaOH treated samples. A change in surface texture can be observed depending on the alkaline attack condition. The profilometry results generated a quantitative evaluation of the surface texture of the metallic substrates after different preparation conditions (Table 2).

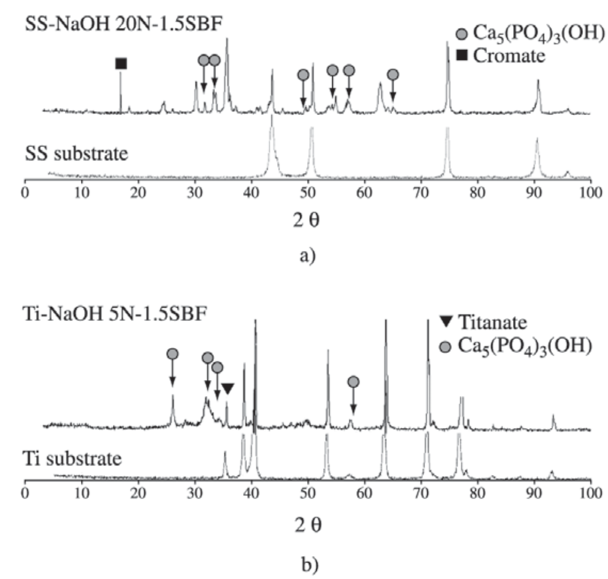

Figure 5. XRD spectra of a) SS treated in NaOH 20N and soaked in 1.5SBF; b) Ti treated in NaOH 5N and soaked in 1.5SBF.

Table 2. Relative variation of central roughness (Sk), central roughness of peaks (Spk) and central roughness of valleys (Svk) of samples treated in NaOH relative to ground samples.

	▲Sk%	▲Spk%	▲Svk%
AISI 316L Stainless Steel in NaOH 5N	35	147	456
AISI 316L Stainless Steel in NaOH 20N	913	1544	1150
ASTM F136 Titanium Alloy in NaOH 5N	122	67	100
ASTM F136 Titanium Alloy in NaOH 20N	2900	1400	4000

It was observed an increase in the relative values of central roughness (S_k parameter) for all the systems treated in NaOH solution, specially the ones treated in the more concentrated NaOH 20N solution. This increase in surface roughness affects the adhesion of the coatings through a micromechanical adhesion mechanism. Previous studies show that the adherence of biomimetic coatings increases with the alkaline treatment of titanium substrates[1,2].

After soaking the treated substrates in 1,5SBF the coatings produced were analyzed by SEM-EDAX and XRD. The results are illustrated in Fig. 4 and Fig. 5. The presence of calcium and phosphorus were detected by EDAX on all samples with a Ca/P ratio ranging from 1.4 to 1.6, indicating the presence of a calcium phosphate layer. In the XRD spectra it was determined the presence of peaks corresponding to a hydroxylapatite phase on all the samples. The definition and intensity of the HA peaks was higher in SS treated in NaOH 20N and Ti treated in NaOH 5N, shown in Fig. 5. The more intense peaks observed on the XRD spectra correspond to the metallic substrates. This indicates that although there is an HA film formed on the samples its thickness is small, once the main contribution to the XRD spectra are still from the substrate. Thin film XRD would allow better characterization of the films obtained. Based on the intensity of HA peaks a more defined HA layer was observed on titanium alloy treated in NaOH 5N and stainless steel treated in NaOH 20N.

4. Conclusions

A calcium phosphate layer could be formed by the biomimetic method on both substrates, Ti and SS, treated with NaOH. The chemical treatment produces an undesirable sodium carbonate layer, which requires an ultrasonic cleaning procedure. The alkali treated Ti and SS substrates develop a sodium titanate or a sodium cromate layer on the surface respectively. It was observed an increase in the relative values of central roughness for samples chemically treated, specially the ones treated in the more concentrated NaOH 20N solution. EDAX and XRD analysis showed the presence of a calcium phosphate layer identified as HA. Apparently, the thickness of this layer is higher on Ti treated in NaOH 5N and SS with the more severe 20N treatment.

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