J Mater Sci: Mater Med (2011) 22:2457–2465
DOI 10.1007/s10856-011-4434-0

Biomimetic calcium phosphate coating on Ti-7.5Mo alloy for dental application

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Received: 6 February 2011 / Accepted: 25 August 2011 / Published online: 10 September 2011

Abstract Titanium and its alloys have been used as bone-replacement implants due to their excellent corrosion resistance and biocompatibility. However, a titanium coating is a bioinert material and cannot bond chemically to bone tissue. The objective of this work was to evaluate the influence of alkaline treatment and heat treatment on the formation of calcium phosphate layer on the surface of a Ti-7.5Mo alloy after soaking in simulated body fluid (SBF). Thirty six titanium alloy plates were assigned into two groups. For group I, samples were immersed in a 5.0-M NaOH aqueous solution at 80°C for 72 h, washed with distilled water and dried at 40°C for 24 h. For group II, after the alkaline treatment, samples were heat-treated at 600°C for 1 h in an electrical furnace in air. Then, all samples were immersed in SBF for 7 or 14 days to allow the formation of a calcium phosphate coating on the surface. The surfaces were characterized using SEM, EDS, AFM and contact angle measurements.

1 Introduction

Titanium and titanium alloys have become very attractive biomaterials due to their light weight, high biocorrosion resistance, biocompatibility and mechanical properties [1, 2]. The relatively low strength commercially pure titanium (c.p.Ti) is currently used in dentistry and the higher strength Ti-6Al-4V alloy is used in a variety of stress-bearing orthopedic applications [3]. However, considerable controversy has been raised about the cytotoxicity of Ti-6Al-4V alloys due to the release of vanadium and aluminum [4].

Despite these excellent properties, titanium and titanium-based alloys are considered to be bioinert, such that when they are inserted into the human body they are generally encapsulated by fibrous tissue and cannot form a chemical bond with bone. However, it is well recognized that calcium phosphate coatings have led to better long-term clinical success rates than uncoated titanium implants [5].

Different methods have been developed to coat metal implants: sol–gel coating, sputter-deposition, electrophoretic deposition, plasma-spraying or biomimetic precipitation [6]. As a result, research to improve the osseointegration of these materials has been undertaken by several authors, including modifications of surface roughness [7], surface treatments [8, 9] and geometries that provide good primary stability, good loading distribution and maintenance of osseointegration [10].

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With surface treatment, it is possible to change the surface features of the titanium dental implant, including its chemical composition, morphology, topography and roughness [11]. The addition of calcium phosphate coatings such as hydroxyapatite ($Ca_{10}(PO_4)_6OH$) to the surface of metallic implants has been used to enhance hard tissue integration, thereby increasing the mechanical stabilization in situ [12]. Currently, metallic implants are coated with hydroxyapatite using a plasma deposition method, that produces nonhomogenous coatings on implants and the high temperatures used in plasma deposition affect the morphology and crystal structure of the deposited film [13]. One of the most promising techniques for producing calcium phosphate coatings is the biomimetic method, which mimics the mineralization process of bone. The biomimetic method utilizes supersaturated aqueous solutions with ionic composition similar to that of human plasma; it allows coating metal implants with apatite crystals [6].

An important requirement for implants designed to replace or interact with bone is a low elastic modulus matching, as closely as possible, that of the surrounding bone tissue. Growing interest has been observed in the development of titanium alloys with different compositions to achieve better performance in terms of biomechanical compatibility [14], such as Ti-29Nb-13Ta-4.6Zr [15], Ti-13Nb-13Zr [16], Ti-6Al-7Nb [17], Ti-10Mo [18–20], Ti-15Mo [21], and Lin et al. [22, 23] developed the binary alloy Ti-7.5Mo, which has a low elastic modulus (55 GPa) and a high strength/modulus ratio.

In the present work, the influence of alkaline treatment and heat treatment on the formation of calcium phosphate layer on the surface of a Ti-7.5Mo alloy after soaking in simulated body fluid (SBF) was evaluated.

2 Experimental procedures

All the materials were prepared from raw titanium (99.9% pure) and molybdenum (99.9% pure) by using an arc furnace under an argon atmosphere. The ingots were then homogenized under a vacuum at 1,200°C for 24 h to eliminate chemical segregation. The resulting samples were finally cold-worked by swaging, producing a 13-mm rod.

Bars of this alloy were machined using a CNC lathe ZIL (CENTUR 30S, ROMY, BR) with a rotation speed of 1,000 rpm to obtain grooved surfaces. Samples were prepared by cutting out discs (13 mm in diameter and 4 mm in thickness) using a Buehler Isomet low-speed diamond. Thirty six titanium alloy plates were assigned into two groups. Group I (alkaline treatment) and group II (alkaline treatment and heat treatment). These samples were ultrasonically cleaned with distilled water and acetone for 15 min and air-dried prior to surface treatment. Machined samples were used as a control group and were not subjected to further surface treatments.

For group I, samples were immersed in a 5.0-M NaOH aqueous solution at 80°C for 72 h. The temperature was maintained by using a water bath. After the 72 h incubation period, the substrates were washed with distilled water and dried at 40°C for 24 h. For group II, after alkaline treatment, samples were heat-treated at 600°C in an electric furnace under an air atmosphere, maintained at this temperature for 1 h and then allowed to cool to room temperature in the furnace.

To test the capability of the material to spontaneously form a calcium phosphate layer in vitro and verify that the deposition of biomimetic Ca–P coatings can be significantly accelerated with increasing concentrations by a factor of five, samples were soaked in 30 ml SBF×5 solutions for 7 or 14 days to induce the formation of a calcium phosphate layer on the sample surface. Kokubo [8] showed that a bioactive titanium surface can be obtained by biomimetic method, via an alkaline treatment in NaOH followed by immersion in SBF (simulated body fluid). By this technique, bone-like apatite coatings could be deposited on titanium implants within 7 days [8]. When the biomimetic method is used to coat metallic implants, one of the critical points is the time, which is considered relatively large to coat the substrate. Studies realized by Barrère et al. [24] indicate that the deposition of biomimetic Ca–P coatings could be greatly accelerated with increasing concentrations by a factor of five (SBF×5). The SBF×5 solution was prepared by dissolving the chemical reagents NaCl (40 g), $MgCl_2 \cdot 6H_2O$ (1.52 g), $CaCl_2 \cdot 2H_2O$ (1.84 g), $Na_2HPO_4 \cdot 2H_2O$ (0.89 g) and $NaHCO_3$ (1.76 g) in 1,000 ml of distilled water and buffering to pH 7.4 with tris-hydroxymethyl aminomethane and hydrochloric acid at 36.5°C [25]. The SBF was refreshed every 48 h to preserve its ion concentration. After soaking, samples were removed from the fluid, washed with distilled water and air-dried for 24 h. The final ionic concentrations of human blood plasma, SBF and SBF×5 are listed in Table 1.

Surfaces were evaluated using a scanning electron microscope (SEM, LEO 1450 VP, Zeiss, Germany) before and after the alkaline treatment (Group I); and soaking in SBF×5 solutions for 7 or 14 days; before and after alkaline treatment plus heat treatment (Group II) and soaking in SBF×5 solutions for 7 or 14 days. Constituents of the samples were analyzed by an energy dispersive X-Ray spectrometer (EDS, Oxford Instruments, Inca Energy Model, UK). In addition, the surface morphologies of the calcium phosphate coatings grown under different conditions were characterized using an atomic force microscope (AFM), VEECO Multimode V, operating in dynamic mode, with a 0.01–0.025-ohm.cm antimony-(n)-doped Si

Table 1 Ion concentrations (mmol/dm^3) of the humam blood plasma compared to those simulated body fluid and SBF×5

Ion concentration	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	$(HPO_4)^{-2}$	$(HCO_3)^-$	$(SO_4)^{-2}$
Human blood plasma	142.0	5.0	1.5	2.5	103.0	1.0	27.0	0.5
SBF	142.0	5.0	1.5	2.5	148.8	1.0	4.2	0.5
5xSBF	710.0	25.0	7.5	12.5	744.0	5.0	21.0	2.5

tip (model TESPW). The scanning area selected was 10 ×10 μm. Quantitative measurements of the surface area and the local root mean square (RMS) surface roughness and average roughness (R_a) were determined using a surface area of 10 ×10 μm. The RMS roughness is defined as the height fluctuations in a given area. R_a is defined as the arithmetic average of the absolute height value of all points in the profile, or the centre-line average height. Measurements of surface area, RMS and R_a roughness were made in three random areas per uncoated specimen and were computed with a surface area and roughness analysis program. The wettability of the coated surfaces was evaluated by water contact angle measurements. The contact angle was obtained using the sessile drop method on a standard Rame-Hart goniometer, model 200. The volume of each drop was 2 μl, and the average value of at least five drops was calculated. Contact angles were statistically analyzed with a *t*-test at a significance level of 0.05.

3 Results and discussion

Figure 1 shows scanning electron micrographs of the surfaces of Ti-7.5Mo substrates machined, surfaces 5.0-M NaOH-treated at 80°C for 72 h, and surfaces NaOH activation with subsequently heat treatment at 600°C for 1 h. The surfaces of untreated samples appeared with several machining marks (Fig. 1a). After immersion in 5.0-M NaOH at 80°C for 72 h the substrates exhibited microporous structures as shown in Fig. 1b. The pore size in this

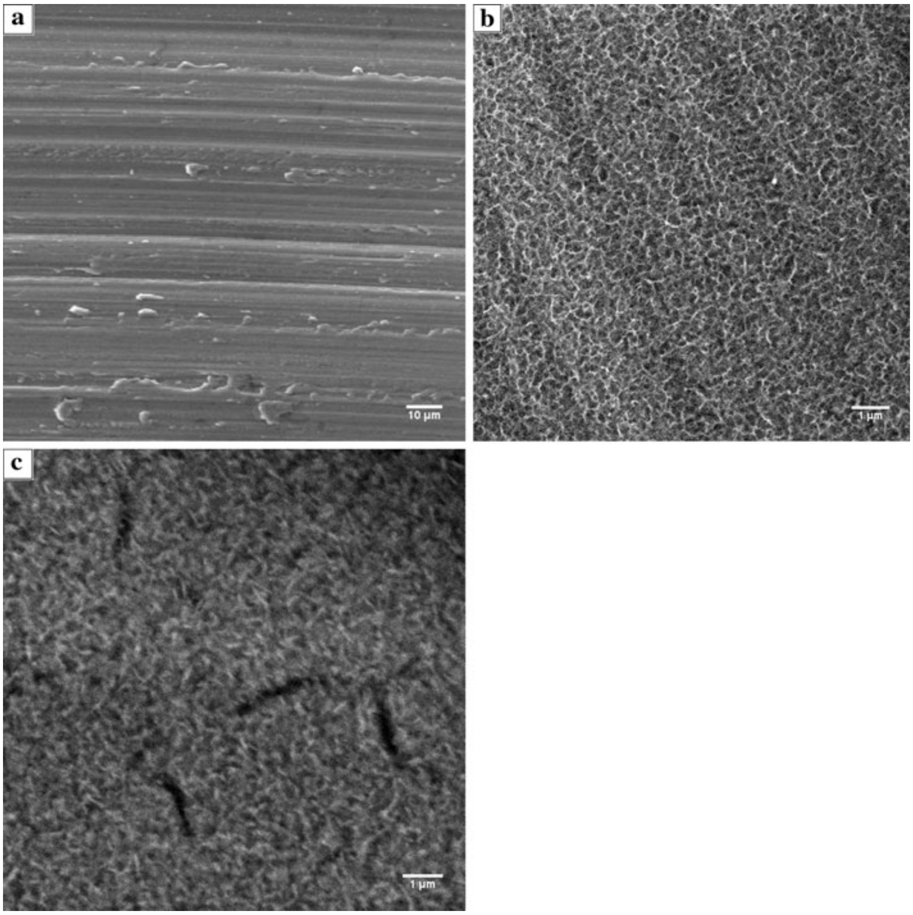

Fig. 1 SEM micrographs of surface morphology of machined control (**a**); alkaline treatment (**b**); alkaline treatment and heat treatment (**c**)

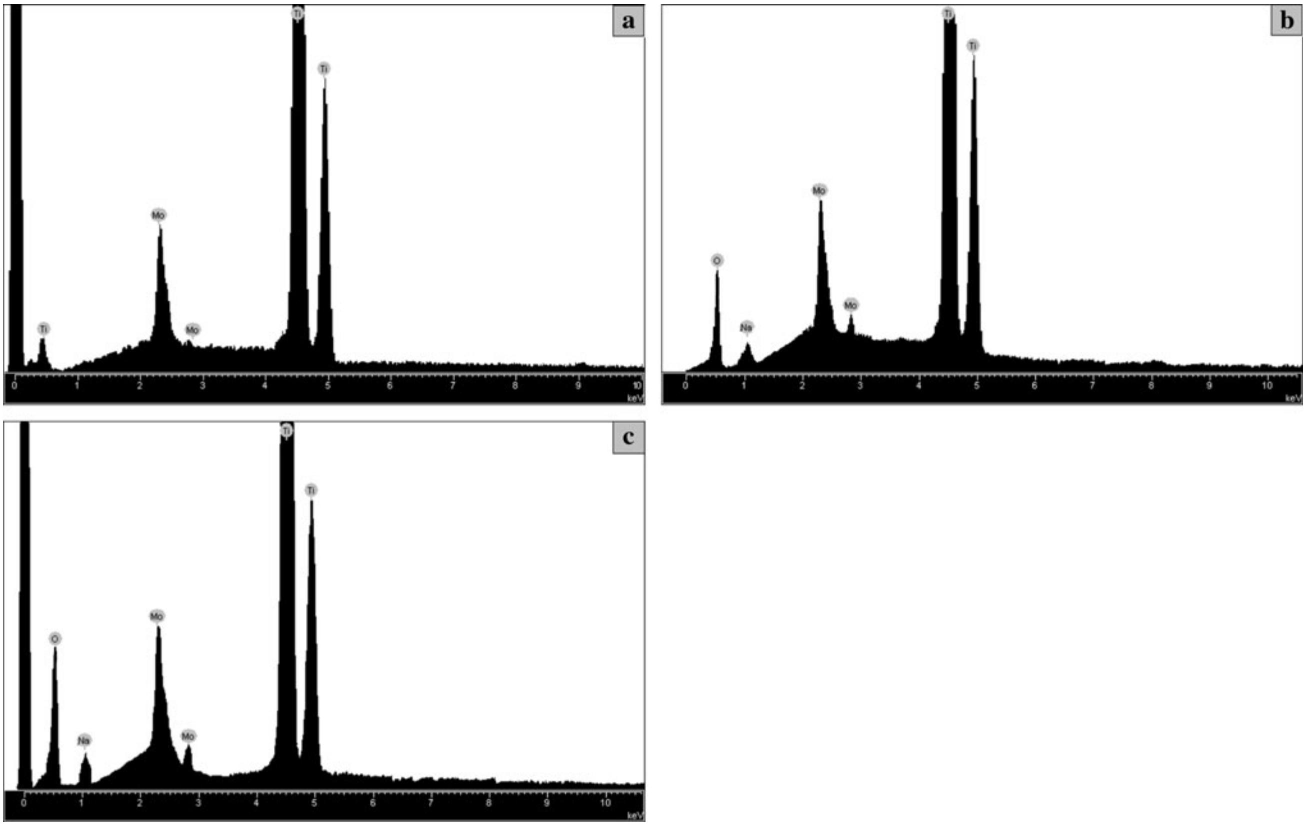

Fig. 2 EDS of machined control (**a**); alkaline treatment (**b**); alkaline treatment and heat treatment (**c**)

Table 2 Amounts of the different elements (Ti-7.5Mo, NaOH-treated and heat-treated)

Element	Ti-7.5Mo		NaOH-treated		Heat-treated	
	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
Na	–	–	0.87	1.24	2.02	2.87
O	–	–	21.21	43.78	32.63	51.34
Ti	92.65	97.72	75.56	54.17	62.54	44.83
Mo	7.35	2.28	2.36	0.81	2.81	0.96
Totals	100.00		100.00		100.00	

structure (50–100 nm), is in agreement with the results reported by Ho et al. [26]. After NaOH activation with subsequently heat treatment at 600°C for 1 h we observed a densified, cavernous-like structure with some cracks, which were probably formed during the heat treatment, that is in agreement with Wei et al. [9]. Chen et al. [12] observed that cracking occurred due to differences in the thermal coefficients of expansion of the substrate versus the surface layer. Jalota et al. [27] reported that drying cracks were expected when such a coating covered the entire substrate surface. According to Kim et al. [28, 29], these microporous structures of metal surfaces appear after alkali treatment and suggest the probable formation of a sodium titanate hydrogel ($Na_2Ti_5O_{11}$ or $Na_2Ti_6O_{13}$). The presence of Na and O is also confirmed by the results of the EDS analysis (Fig. 2b).

Figure 2 shows the EDS spectra of the surfaces of untreated (Fig. 2a), NaOH-treated (Fig. 2b), and NaOH-treated with subsequently heat-treated (Fig. 2c). The EDS analysis of the porous of NaOH-treated samples revealed the presence of O, Na, Ti and Mo (Fig. 2b), thereby indicating the existence of a hydrogel phase consisting of $Na_2Ti_5O_{11}$ or $Na_2Ti_6O_{13}$, and TiO_2. The EDS spectra of NaOH-treated with subsequently heat-treated samples

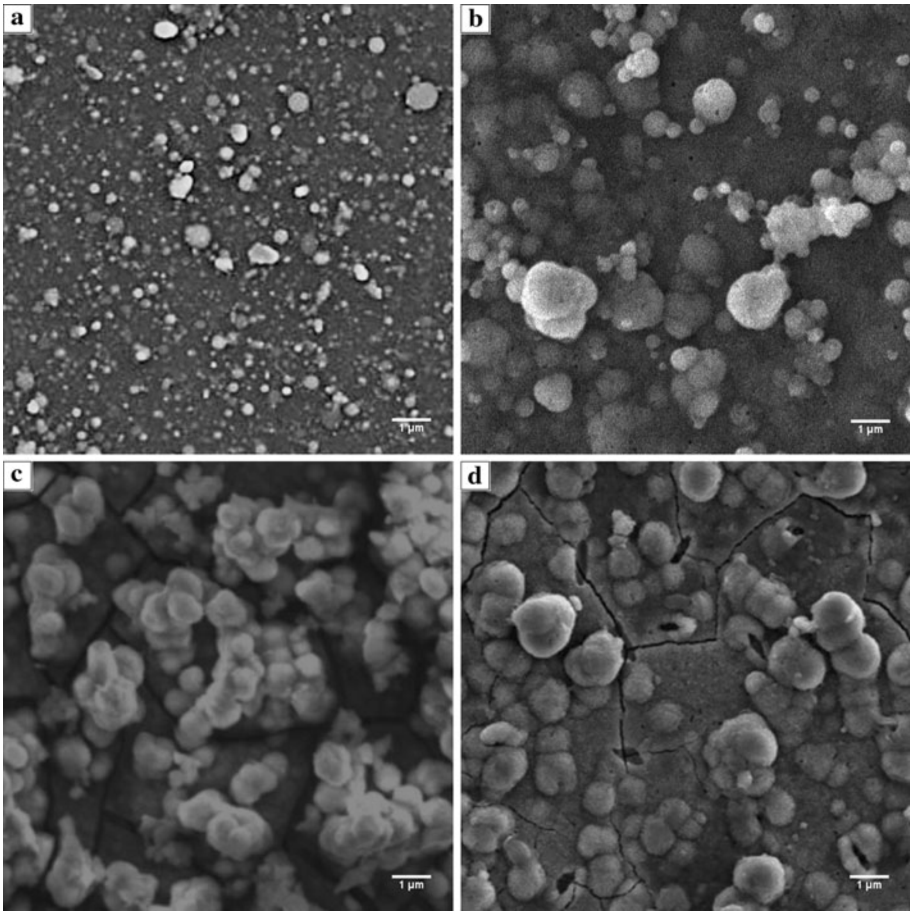

Fig. 3 SEM images of surface morphology of alkaline treatment and soaking in SBF×5 for 7 days (**a**); alkaline treatment and soaking in SBF×5 for 14 days (**b**); alkaline treatment, heat treatment, and soaking in SBF×5 for 7 days (**c**); alkaline treatment, heat treatment, and soaking in SBF×5 for 14 days (**d**)

showed the presence of not only Ti and Mo, but also O and Na on metallic surfaces. It was observed that the intensity of O and Na peaks increased when the heat-treated samples (Fig. 2c), and may be due to the surface structure changes produced by the heat treatment at 600°C. In Table 2 it is possible to observe the amounts of the different elements (Ti-7.5Mo, NaOH-treated and heat-treated). According Wei et al. [9], sintering is very important to improve the adherence of sodium titanate film.

Calcium phosphate precipitation on the surfaces of samples after soaking for different periods in SBF is shown in Fig. 3. For group I, after 7 days in the SBF×5, it can be seen that the calcium phosphates particles present a nano-sized and round morphology were deposited on the surface of specimens (Fig. 3a), whereas, after the same period of time, a greater number of spheroid particles were observed on the surfaces of group II samples (Fig. 3c). Moreover, after 7 days in the SBF, the samples heated-treated at 600°C were mostly covered by a newly layer of calcium phosphate composed of island-like spheroids (Fig. 3c). The final coatings after 14 days of immersion in the SBF (Fig. 3b, d) indicated that a dense and uniform layer was produced on the surfaces; however, it is noteworthy that there were more aggregated island-like spheroids particles with larger diameter were deposited on the surface of the heat-treated Ti-7.5Mo alloy. Figure 3b presents smaller spherulites particles compared to Fig. 3d. The presence of cracks in the calcium phosphate layer on the surfaces of group II samples appear to have formed as a result of cracks present in the sodium titanate film after heat treatment. It is so important to detach that the formation of calcium phosphate layers formation with a similar morphology has been reported for Ti and its alloys, according Rosenberg et al. [30] and Jonasová et al. [31].

The possible mechanism of nucleation and growth of calcium phosphate on alkaline-treated titanium immersed in SBF solution has been proposed as the following [30]. Ti and its alloys form sodium titanate hydrogel layers on their surfaces after NaOH treatments. The sodium titanate layer releases its Na^+ ions into the surrounding fluid via an ion exchange with H_3O^+ in the fluid to form Ti-OH layer. The released Na^+ ions increase the degree of supersaturation of the soaking solution, and the Ti-OH groups interact with the calcium ions in the fluid to form a calcium titanate. The calcium titanate incorporates the phosphate ions, as well as the calcium ions, in the fluid to form calcium phosphate

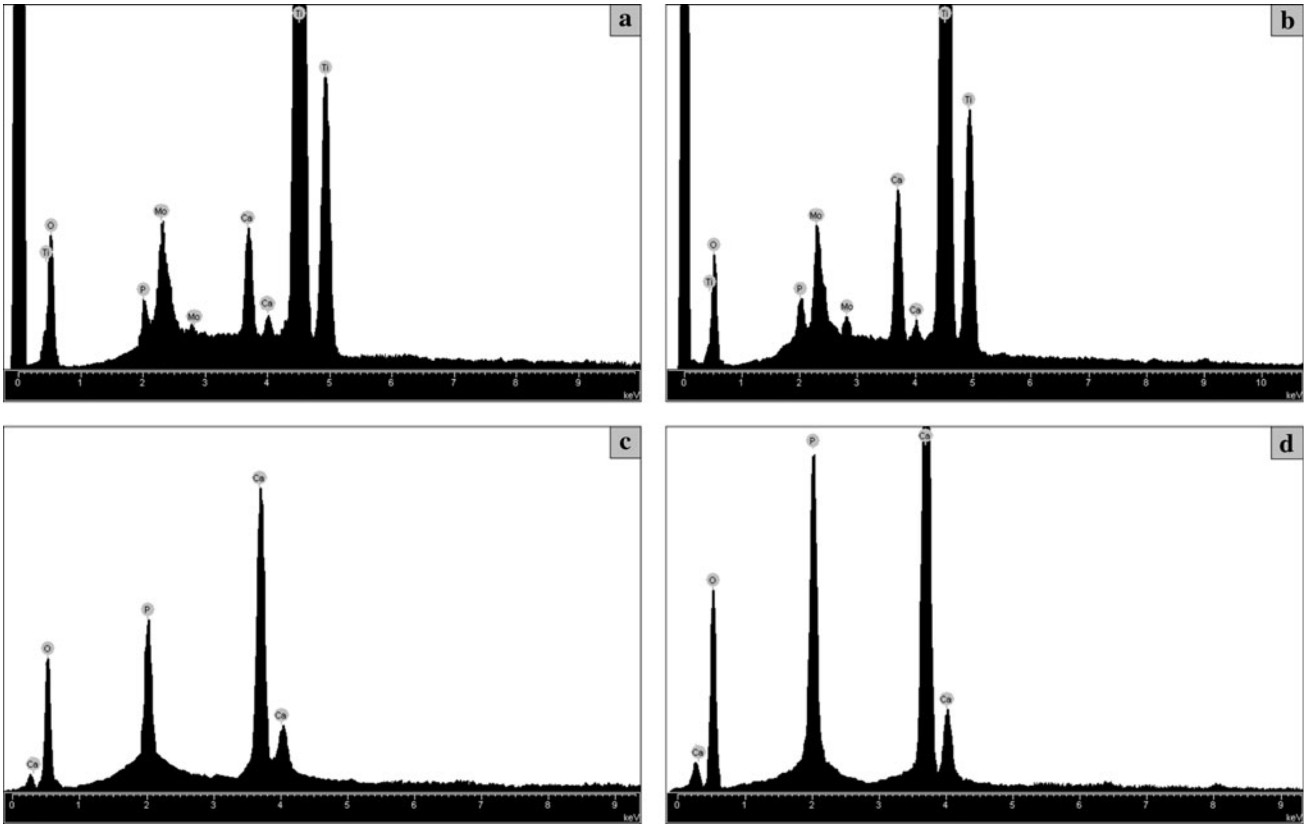

Fig. 4 EDS of surface morphology of alkaline treatment and soaking in SBF×5 for 7 days (**a**); alkaline treatment and soaking in SBF×5 for 14 days (**b**); alkaline treatment, heat treatment, and soaking in SBF×5 for 7 days (**c**); alkaline treatment, heat treatment, and soaking in SBF×5 for 14 days (**d**)

nuclei in the SBF solution. Once formed, the calcium phosphate nuclei grow by consuming the calcium and phosphate ions in the SBF solution.

The results of the EDS analysis of the calcium phosphate Ti-7.5Mo surfaces after being soaked in SBF×5 for 7 and 14 days, are shown in Fig. 4. After this soaking period, all the samples exhibited very intensive peaks of Ca and P, but the intensities of these peaks were greater in the group II samples (Fig. 4c, d) than in group I (Fig. 4a, b). For group I, after 7 days in the SBF×5 (Fig. 1a), it can be seen that these peaks were lower than 14 days of immersion in the SBF×5 (Fig. 4b). As regards the intensity of the peaks of Ti and Mo, after 7 days in the SBF×5 it was higher than 14 days of immersion in the SBF×5 (Fig. 4a, b), and for group II, no peaks of Ti and Mo were detected. The intensity of the peaks of Ti and Mo decreased due to interference from the calcium phosphate deposits after being soaked, thereby indicating that the coatings were thick. Calcium phosphate coating was the thickest for group II likely due to the surface structure changes produced by the heat treatment.

The AFM images (Fig. 5) show in detail the changing surface topography as compared to the machined control surface (Fig. 5a) in the samples with biomimetic treatments (Fig. 5b, c, d, e). The machined control surfaces were smooth and relatively free of scratches (Fig. 5a). The surface topography was altered according to the immersion time in SBF×5, when comparing Fig. 5b with 5c and when comparing Fig. 5d with 5e. All the treated surfaces exhibited roughened oxide topography with sharply defined crests and pits (Fig. 5b, c, d and e). As measured by AFM (Table 2) for Group I, after 7 and 14 days of immersion in SBF×5, the roughness values (RMS, R_a) were increased. For Group II, the roughness values only were increased after 7 days of immersion in SBF×5, while after 14 days of immersion in SBF×5, the roughness values were decreased. This decrease in roughness values is probably related to the increase in the size of calcium phosphate globules, as can be seen in Fig. 3d. In Table 3, is possible to observe that the increase in roughness of the calcium phosphate layer provided an increase in the surface area of 101–114 μm^2 for the same period of immersion (7 days), but for different treatments of the substrate.

In this study, the NaOH treatment improved the hydrophilicity generally used for bioactivity enhancement [32]. Figure 6 shows the average water-contact angles of the Ti-7.5Mo specimens. Distilled water contacted the NaOH-treated samples, and NaOH-treated with subsequently heat-treated at about 61.7° and 45.7° respectively.

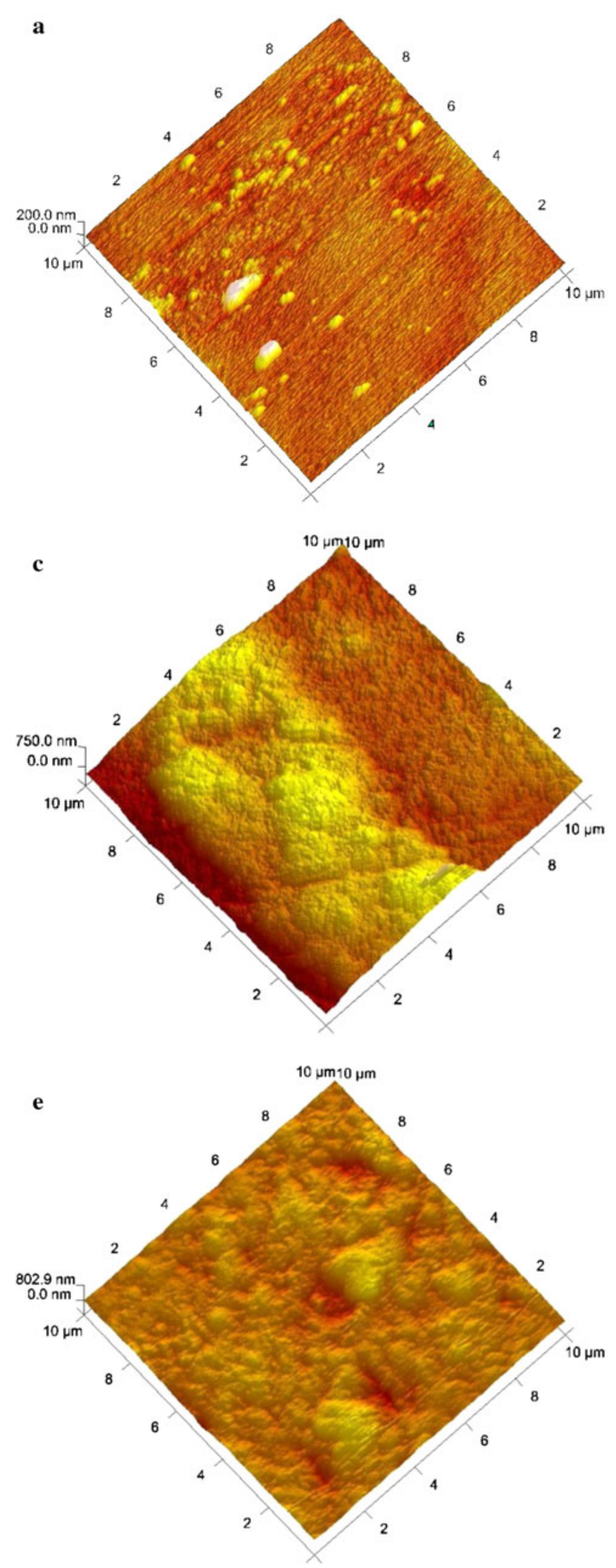

Fig. 5 AFM analyses: **a** machined control; **b** alkaline treatment and soaking in SBF for 7 days; **c** alkaline treatment and soaking in SBF for 14 days; **d** alkaline treatment, heat treatment, and soaking in SBF for 7 days; **e** alkaline treatment, heat treatment, and soaking in SBF for fourteen days

Table 3 AFM roughness measurements for the samples after soaking in SBF for 7 and 14 days (Mean Roughness (R_a), Roughness Mean Square (RMS) and surface area

Group	Immersion time (days)	AFM measured		
		R_a (nm)	RMS (nm)	Surface area (μm^2)
I	7	38.3	46.9	101
	14	53.9	66.8	109
II	7	106	133	114
	14	41.1	51.2	106

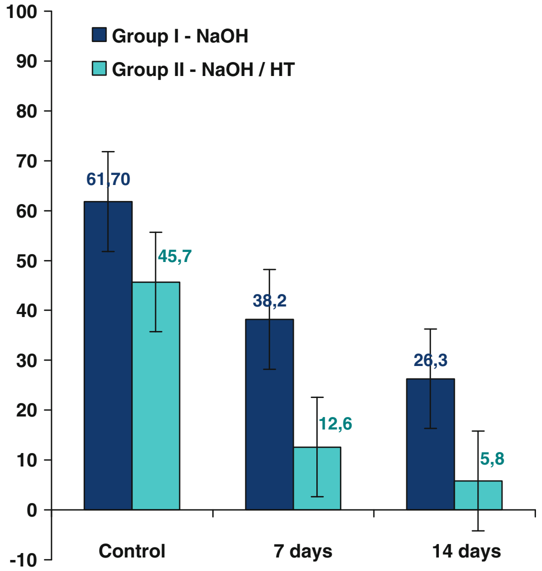

Fig. 6 Average values of contact angles measured after machined control, alkaline and heat treatment, 7 and 14 days for samples subjected to chemical and heat treatments

After these surface treatments, contact angle was decreased according to the immersion time in SBF×5. For Group I after 7 and 14 days of immersion in SBF×5, at about 38.2° and 26.3°, and for Group II, after 7 and 14 days of immersion in SBF×5, at about 12.6° and 5.8° respectively. It is worth noting that among the groups for the same period (7 or 14 days), it was observed that there were significant difference between contact angles values ($\alpha = 5\%$). Of all the test conditions, the Ti-7.5Mo surfaces after NaOH-treated with subsequently heat-treated and immersion in SBF×5 for 14 days had the lowest contact angles. Therefore, the NaOH and heat treatment exhibited great influences on the wettability of the Ti-7.5Mo surfaces.

Surface wettability (hydrophobicity/hydrophilicity) is one of the most important parameters affecting the biological response to an implanted biomaterial. Wettability affects protein adsorption, platelet adhesion/activation, blood coagulation and cell and bacterial adhesion [33, 34]. Highly hydrophilic surfaces seem more desirable than hydrophobic ones in view of their interactions with biological fluids, cells and tissues [35]. Contac tangle measurements give values ranging from 0° (hydrophilic) to 140° (hydrophobic) for titanium implant surfaces [10, 36]. Biomimetic calcium phosphate has a high affinity for biological fluids and therefore, a significantly enhanced the wettability compared to the starting substrates [12]. This result was confirmed in the current investigation. The contact angle results showed that the contact angle of the samples decreased from 61.7° to as little as 5.8° upon the growth of an calcium phosphate layer. According to Lim and Donahue [37], the relationship between the contact angle and wetting occurs in reverse on the same surface. Therefore, a decrease of this angle increases the capacity for surface wettability; this finding was confirmed by the samples coated with biomimetic calcium phosphate.

4 Conclusions

The behavior of Ti-7.5Mo alloy samples submitted to surface treatments was investigated through scanning electron microscopy (SEM), by energy dispersive X-ray spectroscopy (EDS) coupled with the SEM, contact angle analysis and atomic force microscopy (AFM), it was possible to characterize the surface topography of calcium phosphate films with submicron structures.

The NaOH-treated with subsequently heat-treated of Ti-7.5Mo alloy produced films of calcium phosphate that there were more aggregated island-like spheroids particles with larger diameter than the only NaOH-treated samples. Thus, it was found that the heat treatment affected the calcium phosphate formation.

The results indicate a calcium phosphate layer with better hydrophilicity could form on the surface of NaOH-treated with subsequently heat-treated on Ti-7.5Mo alloy, therefore, enhance their surface wettability.

On the basis of the results from EDS analysis after soaking in SBF for 7 and 14 days, all the group I and group II samples exhibited very intensive peaks of Ca and P. Moreover, the intensity of substrate decreased due to interference from calcium phosphate deposits. The results from EDS indicated that the calcium phosphate deposits were greater for the NaOH-treated with subsequently heat-treated of Ti-7.5Mo alloy than for the NaOH-treated.

The alkali treatment of Ti-7.5Mo by NaOH aqueous solutions with subsequently heat-treated can be anticipated to be promising artificial bone substitutes or other hard tissue replacement materials for heavy load-bearing applications due to their wonderful combination of bioactivity, low elastic modulus and low processing costs.

Acknowledgments The authors acknowledge financial support received from FAPESP (Project 00059-4/2007) and Capes.

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