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Characterization of the apatite formation on the surfaces of zirconia and alumina ceramics in body environments.

Amanda Abati Aguiar [1,a], Valter Ussui[1,b], Christiane Ribeiro[1,c],
Marcos A. Scapin[1,d], Dolores Ribeiro Ricci[1,e] Nelson B. de Lima [1,f].

[1]Instituto de Pesquisas Energéticas e Nucleares – Av. Prof. Lineu Prestes, 2242 – Cidade Universitária, SP, Brasil
[a]mandaabati@hotmail.com; [b]vussui@ipen.br; [c]cribeiro@ipen.br , [d]mascapin@ipen.br;
[e]drlazar@ipen.br; [f]nblima@ipen.br.

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Abstract. Induction of an apatite-forming ability on a 100% Y_2O_3-$ZrO_{2,}$ 100% $Al_2O_{3,}$ and 80/20 and 20/80 wt% of zirconia-alumina (Y_2O_3-ZrO_2-Al_2O_3) composite polycrystals via chemical treatment with 5M H_3PO_4 have been investigated. The chemical treatments produced Zr-O surface functional groups, which are known to be effective for apatite nucleation in simulated body fluid. It’s believed that Al-OH surface functional groups are not effective for apatite nucleation. I this work was shown that apatite nucleates in substrate of alumina treat and untreated chemically. This implies that Al-OH functional groups are effective for apatite nucleation.

Introduction

The alumina- tetragonal zirconia ceramics composites are one of relatively good and promising candidate for biomaterial application in bone reconstruction, due to biocompatibility and their mechanical properties that combines high flexural strength with a high toughness. An essential requirement for an artificial material to bond to living bone is via formation of a biological apatite layer on its surface. The bone-bonding ability of a material is often evaluated by examining the ability of apatite to form on its surface in a simulated body fluid (SBF) with ion concentration nearly to those of human blood plasma. *In vitro* studies using SBF, have shown that apatite formation is induced by certain functional sites composed of groups such Si-OH, Ti-OH, Ta-OH and Zr-OH [1,2]. It is believed that Al-OH group do not induce apatite nucleation in body environment [3,4].

Considering the importance of alumina-zirconia as biomaterial, in this work the induction of an apatite-forming ability of a surface chemical treated with aqueous solution of 5M H_3PO_4 of sintered ytria-stabilized tetragonal zirconia polycrystalline (Y-ZrO_2), alumina (Al_2O_3) has been investigated.

Materials and methods

Structural biomaterial of alumina and 3mol% yttria doped zirconia has been prepared by chemical route using the co-precipitation method [5]. Powders were carried to drying at temperature of 80°C for 24 hours, calcinated at 800°C for 1 hour. The sintering was accomplished in the air, in electric type box furnace at 1500^0C for 1 hour for the zirconia stabilized sample (100TZP) and 1600°C for 3 hours for alumina sample (100A). The employed heating rate was from 10°C.min^{-1} until 800°C and 5°C.min^{-1} until the sintering temperature. The samples substrates were immersed in 5ml of 5M H_3PO_4, and kept at 90^0C for 4 days, then washed in pure water and dried at 40^0C for 1 day. After that the samples were immersed in 1.5M SBF in a polystyrene bottle at 37.5^0C. The SBF had ions concentration (Na^+ 213.0, K^+ 7.5, Ca^{2+} 3.8, Mg^+ 2.3, Cl^+ 223.0, HCO_3^- 6.3, HPO_4^{2-} 1.5 and SO_4^{2-} 0.75 mM) nearly equal to those found in human body. The solution of 1.5M SBF was changed by a new one each 3 days. After 3, 6, 15 and 21 days the samples were removed from the SBF, gently washed with ultra pure water, and dried at 37.5^0C. The samples were characterized by X-ray diffraction (XRD- Multiflex; Rigaku Co.) using the Rietveld method [6], scanning electron microscopy (SEM Philips XL-30) and X-ray fluorescence (WDXRF – RIX3000 Rigaku Co.).

Results

Figure 1 shows the XRD patterns of the surfaces of the substrates before and after the treatments with the 5M H_3PO_4. The Rietveld analysis of X-ray diffraction data indicates the formation of cubic, tetragonal and monoclinic phases for zirconia and alpha phase for alumina and that chemical attack leads to cubic to tetragonal and tetragonal to monoclinic transformation.

Table 1 – Substrates composition phase obtained by Rietveld methods

Sample	**Phase composition (wt.%)**			
	α-alumina	**Zirconia tetragonal**	**Zirconia Monoclinic**	**Zirconia Cubic**
100A(H_3PO_4)	99.4	0.32	0.27	--------
100A	99	0.6	--------	--------
100TZP(H_3PO_4)	--------	68.8	22.8	8.3
100TZP	--------	59.2	8.7	32.1

Figure 2 shows the XRD pattern of the samples after immersion in 1.5M SBF. The x-ray diffraction shows, after 15 days immersed in SBF, two broad peaks located at 26° and 32°, characteristic of low crystalline apatite similar to biological apatite. In this case the substrate is not detectable, indicating that the coating of apatite is very thick. No phase transformation was detected in the substrate for the samples immersed until 6 days.

Table 2 – Layer thickness and Ca/P atomic ratio of apatite formed on substrate.

Sample	thickness [μm]-Ca/P 3 days 1.5SBF	thickness [μm]-Ca/P 6 days 1.5SBF	thickness [μm]-Ca/P 15 days 1.5SBF	thickness [μm]-Ca/P 21 days 1.5SBF
100A	0.20 - 0.52	2.13 - 1.46	365.3 - 1.80	381.5 - 2.06
100A (H_3PO_4)	0.25 - 0.68	2.76 - 1.42	383.4 - 1.95	386.7 - 2.19
100TZP	0.37 - 0.71	1.84 - 1.47	177.4 - 1.82	192.2 - 2.12
100TZP (H_3PO_4)	0.06 - 0.52	2.01 - 1.51	171.4 - 2.31	201.4 - 2.21

The apatite thickness and the Ca/P ratio after biomimetic recovery were obtained by X-ray fluorescence measurement. The thickness of the deposited apatite increases with time for all composition on the substrate treated and untreated chemically. The analyses of Ca/P ratio indicates that after 3 days a P-rich phase is formed, with ratio between 0.5-0.7. After 6 days this ratio increases to 1.4-1.5, increasing to 1.8-2.3 when thickness is greater than 170μm.

The Figure 3 presents the SEM micrographs of the apatite formed on substrate of alumina untreated chemically after 3 days immersed in SBF, showing particles and agglomerates deposited scarcely on the surface of the substrate. The particles size is around 2μm and the agglomerates size range is 4μm to 10μm. The substrate treated with 5M H_3PO_4 for 3 days presents mainly agglomerates with size range of 4μm to 10μm. The thickness measured by XRF shows this little difference. The density of the apatite agglomerates increase with immersion time in SBF. After 6 days, the thickness increase to 2.13μm and 2.8μm for untreated and treated samples respectively, and is possible to observe in the micrograph the increasing of the agglomerates density with particle size range of 5μm to 15μm. After 15 and 21 days the surface is covered with apatite layer for both, treated and untreated substrates

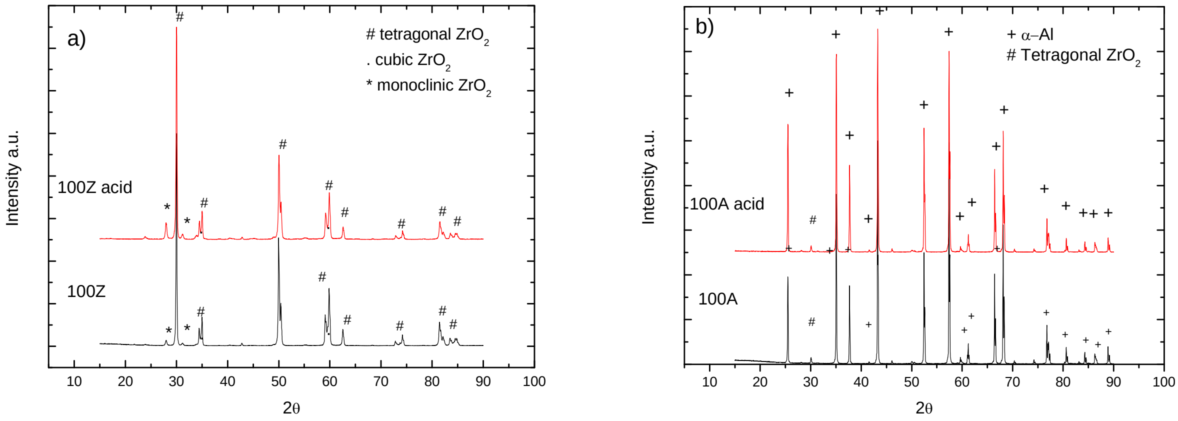

Figure 1- X-ray diffraction patterns of the surfaces of the sample (a) alumina and (b) zirconia untreated chemically and treated with 5M H_3PO_4 .

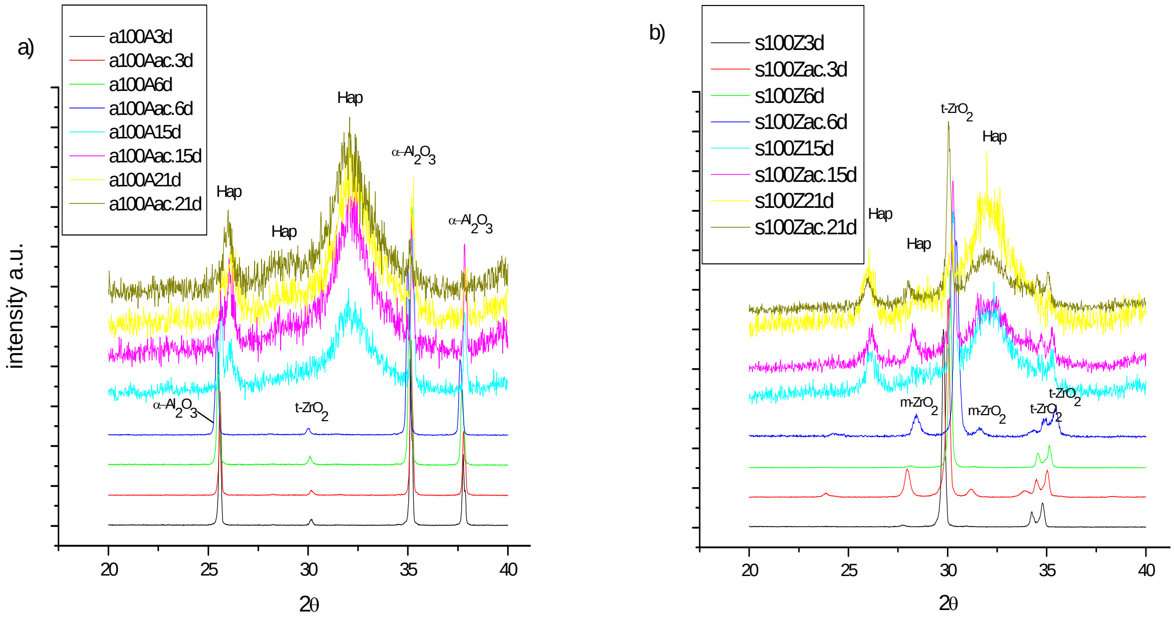

Figure 2- X-ray diffraction patterns of the surfaces of the sample (a) alumina and (b) zirconia untreated chemically and treated with 5M H_3PO_4 soaked in 1.5 SBF after various periods

The sample 100TZP without chemical treatment presents apatite particles with sizes from 0.5 to 2µm dispersed on the substrate. The sample 100TZP with chemical treatment presents apatite particles with sizes around 2µm and apatite agglomerates with sizes range of 6 and 8µm with homogeneous distribution. After 15 and 21 days the surface is covered with apatite layer for both, treated and untreated substrates.

These results are in agreement with the results presented in the Table 2, whose equivalent thickness of apatite is around 0,6µm for samples immersed for 3 days and around 2µm for samples immersed in SBF for 6 days. At this stage, the samples attacked with acid present more agglomerates than particles of apatite and are thicker than samples without previous attack, which presents more particles than agglomerates.

After 15 and 21 days immersed in SBF all samples with thickness greater than 170µm presents micrograph quite similar to that presented in figure 3A/B and 4A/B, meaning that the whole surface of the substrate were covered with apatite layer

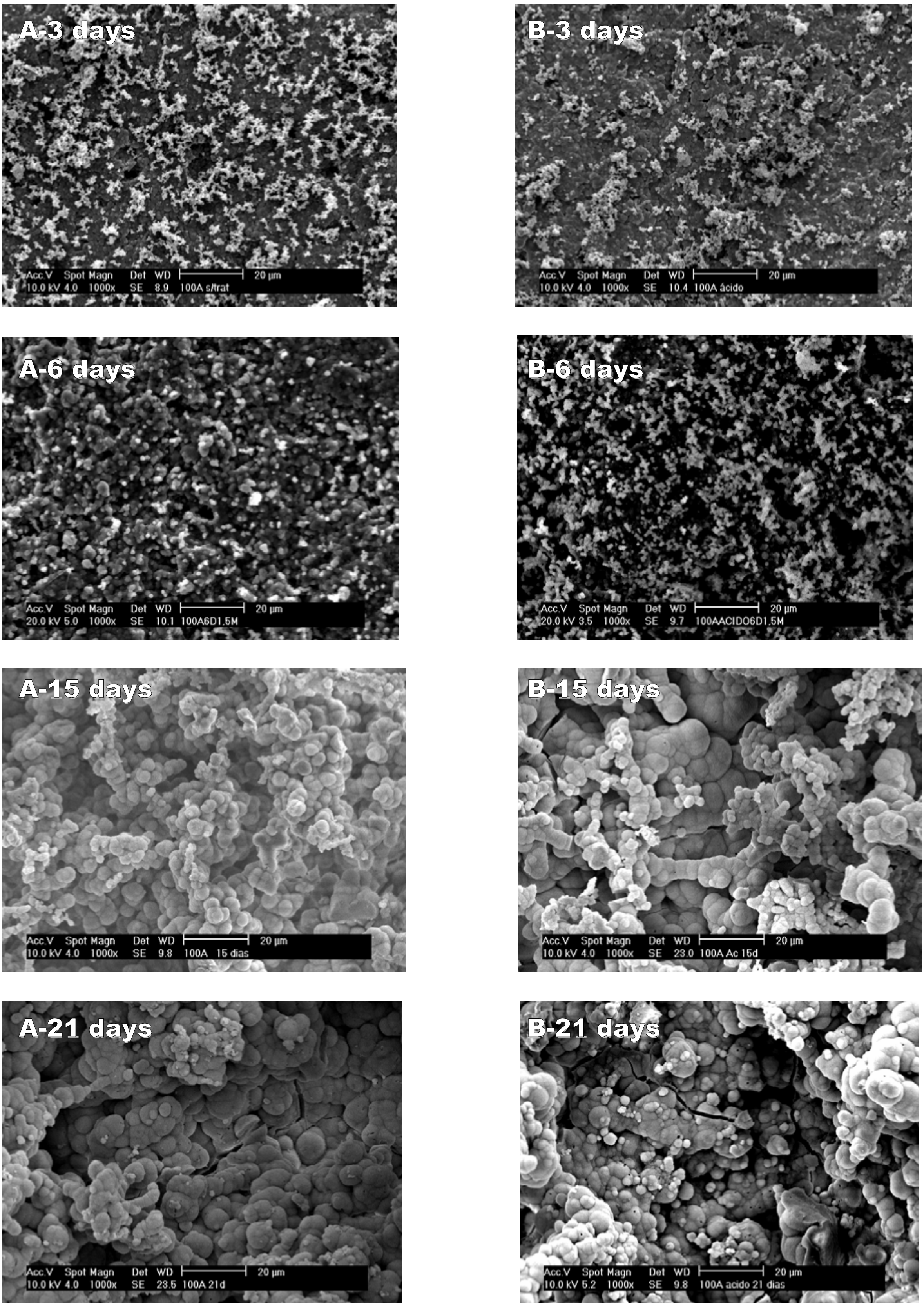

Figure 3- SEM photographs of the surfaces of the sample 100A of (A) untreated chemically and (B) treated with 5M H_3PO_4 soaked in 1.5 SBF after various periods.

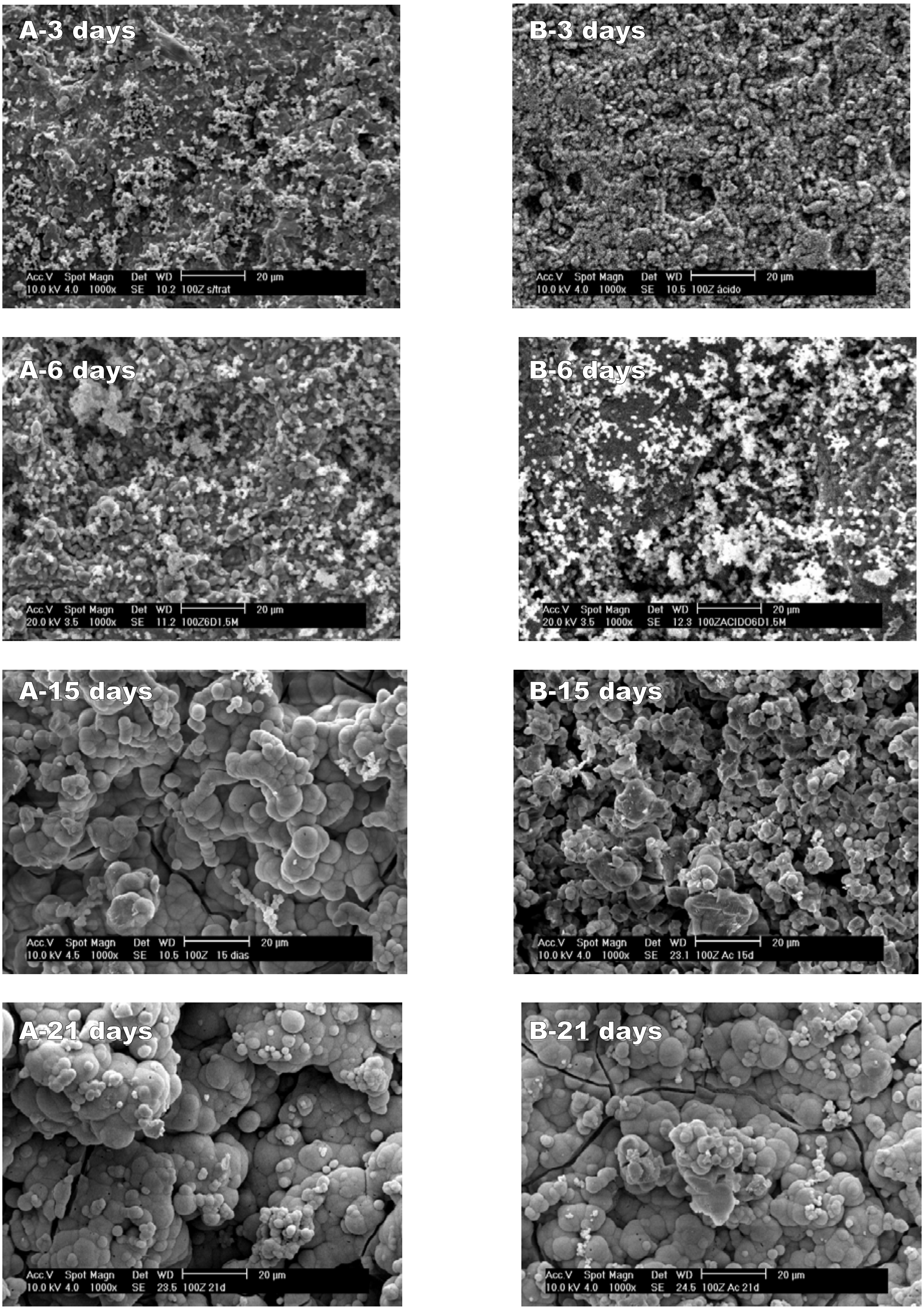

Figure 4- SEM photographs of the surfaces of the sample 100TZP of (A) untreated chemically and (B) treated with 5M H_3PO_4 soaked in 1.5 SBF after various periods.

Discussion

The presence of cubic phase in sample containing zirconia was also observed by other autors[7,8]. Matsui[8] showed that the cubic phase starts to appear at 1300^{0}C for samples with 2.9 mol% Y2O3-ZrO$_2$. This fact is related with yttrium segregation between boundaries grains, showing that cubic phase region started to be transformed from the grain boundary.

The zirconia is sensitive to low temperature aging and it is also associated to roughening of the surface. Our samples were not polished before chemical treatments and present ra roughness value around 3μm, then an acceleration of the degradation with chemical treatment is expected.

The results show that alumina and zirconia possess an apatite-forming ability in SBF solution. Despite of previous articles [1,2,3,4] believed that Al-OH do not induce apatite nucleation, our results obtained with samples 100A (treat and untreated chemically) shows the opposite. The thickness of the apatite layer in samples 100A is greater than samples containing zirconia. The Zr-OH and Al-OH groups are assumed to serve as the site for apatite nucleation. Once the apatite nuclei are formed on the substrates, they grow spontaneously by consuming the calcium, phosphate, and hydroxide ions in SBF, because SBF is highly supersaturated with respect to apatite. After 3 days immersed in SBF, a compound rich in phosphate is formed with Ca/P low. Increasing the time of immersion in SBF, the Ca/P ratio increases until get values between 1.9 and 2.3.

The mechanism of apatite formation is the nucleation of small and dispersed no spherical particles. The SEM micrograph presented in the figure 3A/B and 4A/B, 3 days soaked in SBF, illustrate this fact. After the nucleation, increasing the time of immersion in SBF, the precipitation of calcium, phosphate and hydroxide ions continues and the particles turn agglomerates, according to figure 3B and 4B with 6 days soaked in SBF. After this step, the saturation occurs and the agglomerate becomes spherical particles connecting each other forming larger agglomerates and hence forming a layer that cover the whole surface(figures 3A/B and 4A/B, for 15 and 21 days soaked in SBF).

After the formation of the apatite layer, the same process restarts, repeating the nucleation process: agglomeration, spherical particles formation and coalescence, forming new apatite layer according to figure 3B and 4B for 21 days soaked in SBF.

The above results (Ca/P, thickness and micrograph) show that the influence of chemical treatment to apatite forming ability in the SBF is almost nil in comparison to untreated material.

Conclusions

The Zr-OH and Al-OH groups are assumed to serve as the site for apatite nucleation

The influence of chemical treatment with 5M H3PO4 to apatite forming ability in the SBF is almost nil in comparison to untreated material**.**

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