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# Bone-like apatite coating on Mg-PSZ/$Al_2O_3$ composites using bioactive systems

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**Abstract** A biomimetic method was used to promote bioactivity on zirconia/alumina composites. The composites were composed of 80 vol% Mg-PSZ and 20 vol% $Al_2O_3$. Samples of these bioinert materials were immersed in simulated body fluid (SBF) for 7 days on either a bed of wollastonite ceramics or bioactive glass. After those 7 days, the samples were immersed in a more concentrated solution (1.4 SBF) for 14 days. Experiments were also performed without using a bioactive system during the first stage of immersion. A bone-like apatite layer was formed on the surface of all the materials tested, using wollastonite the bioactive layer was thicker and its morphology was close to that observed on the existing bioactive systems. A thinner apatite layer consisting of small agglomerates was obtained using bioactive glass. The thickness of the ceramic layers was within the range of 15 to 30 $\mu$m.

## 1 Introduction

The interest of using zirconia as a ceramic biomaterial is related to its good chemical and dimensional stability, and to its high mechanical strength and fracture toughness [1]. The current main application for this ceramic is in the manufacture of synthetic femoral heads for total hip replacement [2].

Zirconia ($ZrO_2$) has three polymorphic transformations: monoclinic (M), cubic (C) and tetragonal (T). At room temperature pure zirconia is monoclinic. This phase is stable up to 1170°C. Above this temperature it transforms into tetragonal phase and then into cubic phase at 2370°C. During the cooling, the T-M transformation is associated to a volumetric expansion of approximately 3–5%, which generates stresses that originates cracks in the ceramics [3]. In order to avoid such transformation, small amounts of dopants, like MgO, CaO or $Y_2O_3$, are added to partially stabilize the cubic phase at room temperature [1].

Despite the excellent mechanical properties of pure and partially stabilized zirconia, it presents the disadvantage of undergoing a phase transformation when exposed to aqueous environments at low temperatures (100–400°C). This phase transformation has a detrimental effect on the mechanical properties. Since biomaterials must be autoclave-sterilized under such conditions, it is important to use materials immune to this degradation [4, 5]. It has been reported in the literature that zirconia/alumina composites exhibit a high resistance to this low temperature degradation [6, 7].

Zirconia and alumina ceramics are classified as bioinert materials, which means that they will not bond chemically to living tissue. On the other hand, bioactive ceramics (Bioglass®, wollastonite, hydroxyapatite) are able to bond to living bone via the formation of a bone-like apatite layer on their surface [2, 8]. Since bioactive ceramics have poor mechanical properties, they are used as coatings for other biomaterials with better mechanical performance.

Hydroxyapatite (HA) coatings are widely studied due to its similarity with the mineral phase of bone. One of the techniques used for obtaining HA coatings is the biomimetic process, which consists mainly in the deposition of apatite on the surface of a substrate immersed in simulated body fluids (SBF, 1.4 SBF, 1.5 SBF, 5 SBF). As reported previously [9] the formation of apatite was enhanced if the procedure was performed using a re-immersion method in which the SBF was periodically replaced to maintain a high ionic concentration. Moreover, if a bioactive glass bed is used as a calcium

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supplier during the first phase of the immersion, the apatite nucleation is more effective [10].

In the present work, the effect of the presence of wollastonite or bioactive glass as a calcium ion supplier, on the apatite formation on the surface of a zirconia/alumina composite was investigated.

## 2 Materials and methods

Zirconia/alumina composites (80 vol% Mg-PSZ/20 vol% $Al_2O_3$) were prepared using reagent-grade magnesium oxide stabilized zirconia (Stanford Materials Corp., USA) and alumina (Sasol, USA) with a particle mean size of 0.5 and 0.4 $\mu$m, respectively. The powder mixture was ball-milled in a polyethylene jar with alumina balls for 1 h in acetone. The zirconia/alumina slurries were dried and disk-shaped by uniaxial pressing at 100 MPa for 15 s.

The disks obtained were sintered in air for 2 h at 1550°C. The heating rate used was 10°C/min up to 1000°C and 5°C/min to the final temperature, and the cooling rate was 10°C/min. The sintered materials were biomimetically treated using simulated body fluids and either wollastonite powder (Gosa, S.A.) or bioactive glass. Experiments were also performed without using a bioactive system.

The bioactive glass was prepared by mixing reagent-grade silica, sodium carbonate, calcium oxide and phosphoric pentoxide. The powder mixture was ball-milled in a polyethylene jar with alumina balls for 1 h. The mixture was melted and homogenized in an alumina crucible at 1350°C in an electric furnace for 3 h and poured on a metallic plate. The glass was crushed in a laboratory planetary-type agate ball-mill and sieved through a #400 mesh (<38 $\mu$m). Particle size distribution analysis of the bioactive glass and wollastonite powder were performed by laser diffraction (Coulter). Chemical analysis of both the glass and the wollastonite powder were undertaken using atomic absorption spectroscopy and wet-way methods.

For the biomimetic process two simulated body fluids, one with an ionic concentration nearly equal to that of human blood plasma (SBF) and other 40% more concentrated (1.4 SBF), were used (Table 1). The solutions were prepared dissolving reagent-grade sodium chloride (NaCl), sodium hydrogen carbonate ($NaHCO_3$), potassium chloride (KCl), dipotassium hydrogen phosphate trihydrate ($K_2HPO_4$ & $\cdot 3H_2O$), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) and sodium sulfate ($Na_2SO_4$) in deionized water and buffered to pH 7.4 with tris(hydroxymethyl)-aminomethane and 1N HCl at 36.5°C [11].

The substrates were washed with acetone and deionized water, and then immersed in 150 ml of SBF or 1.4 SBF at 36.5°C using a re-immersion method. This method consisted of immersing the ceramic substrates in SBF for 7 days with or without the presence of a bed of wollastonite or bioactive glass. Then, the SBF was replaced with 1.4 SBF and the bioactive material (wollastonite or bioactive glass) was removed in the corresponding cases. This solution was replaced with fresh 1.4 SBF after one week. This re-immersion procedure is shown in Fig. 1. The pH of the SBF was measured at different intervals during the first seven days of immersion. At the end of the immersion periods, the substrates were removed from the bottles, gently washed with deionized water and dried at room temperature.

The surface of the biomimetically-treated samples was coated with a thin layer of carbon before examination under a scanning electron microscope (JSM 6300, Jeol, Japan) with an energy dispersive X-ray spectroscopy attachment (EDS). The SEM and EDS analyses were performed at an accelerating voltage of 20 or 30 keV. To obtain good quality SEM images the working distance was varied between 39 and 43 mm. The phases present on the biomimetically-treated samples were identified by X-ray diffraction (XRD) (X'Pert, Philips, Holland) at a current of 30 mA and a voltage of 40 kV. The XRD analyses were performed under the following conditions: $\lambda = 1.54056$ Cu, reflection angle ($2\theta$) from 10 to 80° and a step rate of 0.025° $2\theta$/s.

## 3 Results

Table 2 shows the chemical analysis of the bioactive glass obtained. The chemical composition of the glass differs slightly from that of Bioglass® 45S5. However, this is within the specified range for bioactive glasses [2, 12]. The chemical composition of the wollastonite used was 49.06 and 47.70 mol% of $SiO_2$ and CaO, respectively. The mean diameters of the bioactive glass and wollastonite particles were 9.249 and 11.28 $\mu$m, respectively.

The variations of pH for the SBF during the re-immersion procedure, without any bioactive system (c), with a wollastonite bed (b) and with a bioactive glass bed (a), are shown in Fig. 2. The pH increased with time of immersion.

**Table 1** Ion concentration of SBF, 1.4 SBF and human blood plasma.

| | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $Cl^-$ | $HCO_3^-$ | $HPO_4^{2-}$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|---|
| SBF | 142 | 5 | 2.5 | 1.5 | 148.8 | 4.2 | 1 | 0.5 |
| 1.4 SBF | 198.9 | 7 | 3.5 | 2.1 | 208.32 | 5.88 | 1.4 | 0.7 |
| Blood plasma | 142 | 5 | 2.5 | 1.5 | 103.0 | 27.0 | 1 | 0.5 |

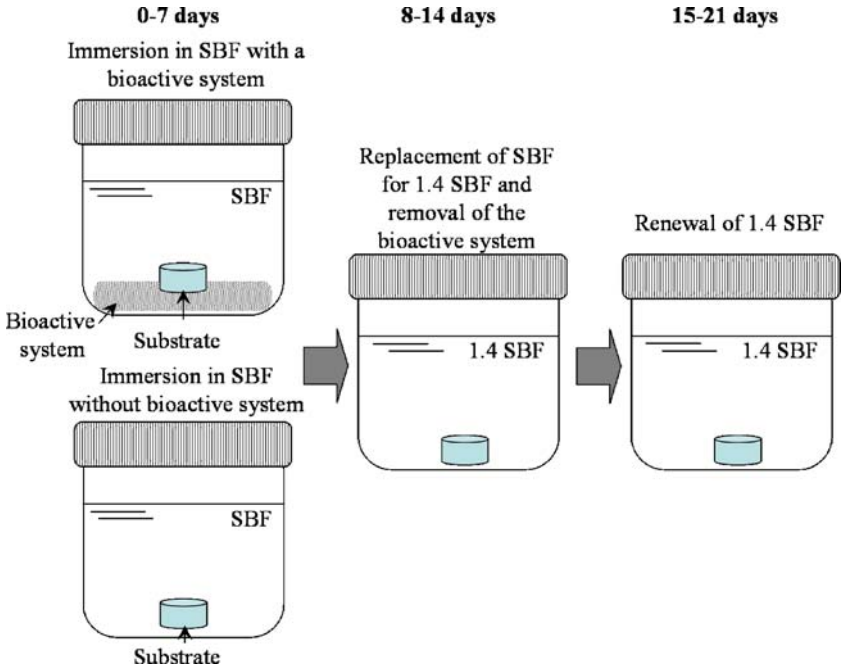


**Fig. 1** Schematic representation of the re-immersion method

**Table 2** Chemical analysis of the bioactive glass obtained.

| | $SiO_2$ | CaO | NaO | $P_2O_5$ | $Al_2O_3$ |
|---|---|---|---|---|---|
| Bioglass 45S5® [2] | 45 | 24.5 | 24.5 | 6 | – |
| Bioactive glass | 46.58 | 23.06 | 24.53 | 4.93 | 0.9 |

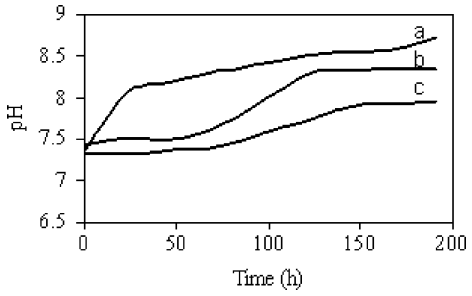


**Fig. 2** Behavior of pH during the first 7 days of immersion in SBF: (a) without bioactive system, (b) with a wollastonite bed and (c) with a bioactive glass bed

This increase may indicate that an ionic exchange is taking place.

Figure 3 shows the surface of the composite after 21 days of immersion (re-immersion method) without using a bed of bioactive system (Fig. 3a), using a bed of wollastonite powder (Fig. 3b) and using a bed of bioactive glass (Fig. 3c). A homogeneous and thick layer was formed on the surface of the three different samples. According to the EDS spectra, the main elements detected were P, Ca and O. The peaks of lower intensity corresponding to Na, Mg and Cl ions may be due to the presence of these elements in the simulated body fluids since, according to the literature [2, 13], the apatite formed in SBF is a partially-substituted apatite with other ions in minor contents. Additionally, a recent work has reported that the presence of magnesium in SBF leads to Mg-containing apatite layers on bioactive systems [14]. Elements corresponding to the substrates, such as Al and Zr, were not detected by EDS. Using bioactive glass during the first 7 days of immersion, the ceramic agglomerates consisted of much smaller particles and the topography was highly irregular (Fig. 3c). The SEM image of the sample immersed on a bed of wollastonite (Fig. 3b) shows the presence of smaller ceramic particles that may grow as the immersion time increases. The morphology of this layer (Fig. 3b), and that of the layer formed on the sample immersed with no bioactive system (Fig. 3a), closely resembled the morphology of the layer formed on the existing bioactive systems [12, 13].

The Ca/P ratios of the ceramic layers, shown in Fig. 3, were calculated from the EDS analysis and they are shown in Table 3. In all the cases, the Ca/P ratio was lower than that of hydroxyapatite (1.67). As mentioned above, the apatite obtained using SBF contains other elements in minor concentrations and the bioactive layer shows low crystallinity and a defective structure [2, 13]. Ca ions may be partially substituted for Mg, Na and Cl. The lowest Ca/P ratio was obtained using a wollastonite bed during the first stage of the biomimetic process, (1.45). This value is within the range of the Ca/P ratio for the bone apatite (1.2–1.5) [2].

Figure 4 shows the XRD patterns of the substrate before the immersion in simulated body fluids (Fig. 4a) and after the biomimetic treatment without using a bed of bioactive system (Fig. 4b), on a bed of wollastonite (Fig. 4c) and on a bed of bioactive glass (Fig. 4d). As it can be observed, new peaks at 25.9 and 31.7° 2 $\theta$;, corresponding to apatite, were detected for all the biomimetically-treated samples. The

**Table 3** Ca/P ratio of the ceramic layer formed on the Mg-PSZ/$Al_2O_3$ composites.

| | Ca/P ratio |
|---|---|
| Immersion in SBF with no bed of bioactive system | 1.57 |
| Immersion in SBF on a bed of wollastonite | 1.45 |
| Immersion in SBF on a bed of bioactive glass | 1.56 |

intensity of the peaks corresponding to zirconia decreased for all the samples treated and the peak corresponding to alumina is no longer detected. On the samples immersed in SBF on a bed of wollastonite, the peaks corresponding to zirconia were hardly detected. Furthermore, a more defined apatite peak can be observed in the pattern shown in Fig. 4c. This may indicate that a thicker apatite layer can be formed using wollastonite ceramics.

It has been reported that bioceramic materials more likely induce octacalcium phosphate (OCP) or an OCP-like structure in both simulated and real body solutions [15, 16]. The

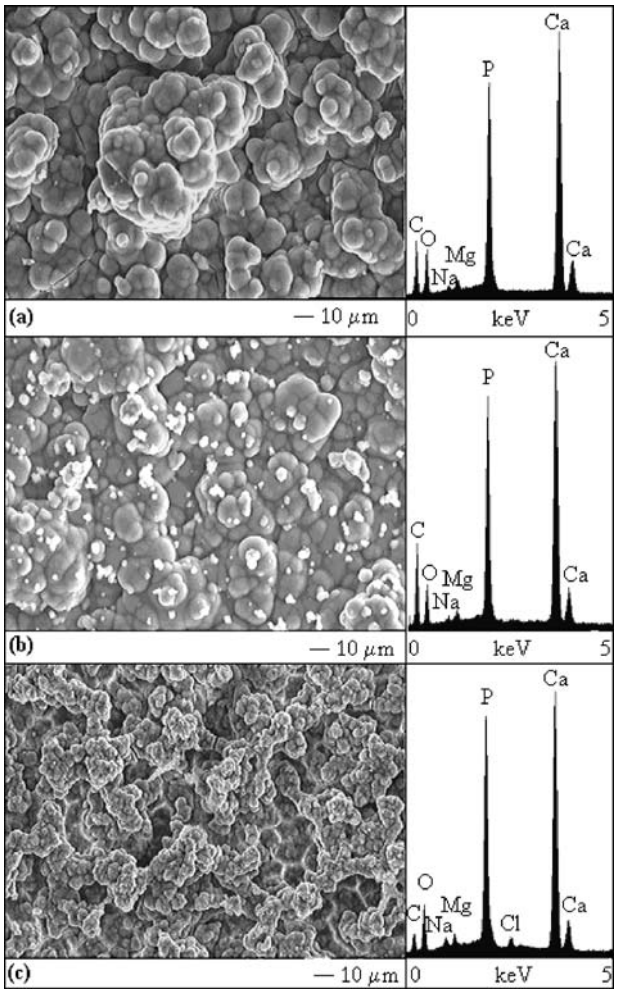


**Fig. 3** SEM photographs and corresponding EDX spectra of the composite surface after 21 days of the re-immersion method: (a) without bioactive system, (b) with a wollastonite bed and (c) with a bioactive glass bed

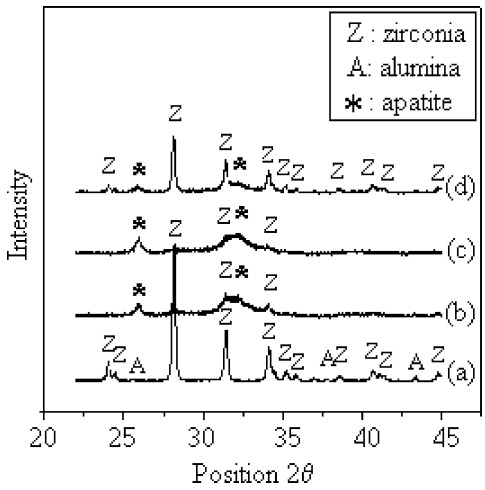


**Fig. 4** XRD patterns of the composite before the biomimetic process (a) and after 21 days of the re-immersion method: (b) without bioactive system, (c) with a wollastonite bed and (d) with a bioactive glass bed

OCP-like structure may accept ion substitution to a certain level. This may also explain the presence of peaks corresponding to Mg, Na and Cl in the EDX spectra. The Ca/P ratios are close to that of (OCP) however, the specific XRD pattern was not detected.

Figure 5 shows the EDS analysis of Ca, P, Zr and Al of a cross-section of the composite immersed in SBF using no bioactive system (Fig. 5a), a bed of wollastonite (Fig. 5b) and a bed of bioactive glass (Fig. 5c). The line scan analysis was performed along the white line starting in the specimen at a distance of 5 to 10 $\mu$m from the substrate surface. The Zr content decreases, along the substrate, when the linear analysis scans alumina particles. The Al content increases when alumina particles are scanned. As approaching the surface, the Zr content decreases dramatically and the Ca and P contents increase. The variations in the Zr and P content through the apatite layer are due to the proximity of their EDS characteristic peaks. The thickness of the apatite layer was, approximately, of 20 $\mu$m on the sample treated with no bioactive system (Fig. 5a), 30 $\mu$m on the sample immersed on a bed of wollastonite (Fig. 5b) and 15 $\mu$m on the sample immersed on bioactive glass (Fig. 5c). Thus, the thickest apatite layer was formed using wollastonite ceramics during the first seven days of immersion in SBF, while the thinnest layer was observed using bioactive glass. This is in agreement with the corresponding XRD patterns shown in Fig. 4.

## 4 Discussion

The results obtained indicate the feasibility to obtain bioactive zirconia/alumina composites using a biomimetic method consisting in the immersion of the substrates in SBF for 7 days, followed by the immersion of the samples in 1.4 SBF

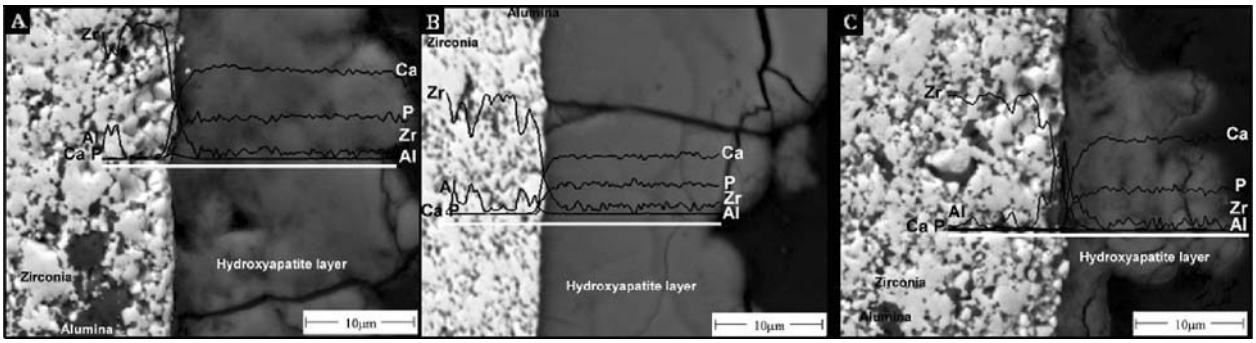


**Fig. 5** EDS analysis of a cross-section of the composite after 21 days of the reimmersion method: (a) without bioactive system, (b) with a wollastonite bed and (c) with a bioactive glass bed

for 14 days (re-immersion method). As stated in the literature [17], the re-immersion method in the biomimetic process promotes the apatite nucleation on the substrate during the first 7 days of immersion in SBF and then, in the second immersion period, the subsequent crystal growth by consuming $Ca^{2+}$ and $P^{5+}$ from the 1.4 SBF.

In addition, if the sample is immersed in SBF on a bed of wollastonite powder during the first stage of the immersion period, the thickness of the apatite layer and thus, the rate of apatite formation, increase. In this case, the apatite formation is mainly due to the $Ca^{2+}$ ions that are released into the simulated body fluid from the wollastonite leading to the increase of the supersaturation degree of the fluid with respect to apatite by increasing pH. The apatite formation occurs on both, the bioinert substrate and the bioactive system itself. The behavior of pH with time of immersion indicates that the increase of pH is higher for the SBF corresponding to the samples immersed on a bed of bioactive glass (Fig. 2a), using this material, $Na^{+}$ and $Ca^{2+}$ are exchanged by $H^{+}$ [18], whereas using wollastonite, the exchange occurs only between $Ca^{2+}$ and $H^{+}$ [19]. Furthermore, as an amorphous material, the bioactive glass has a more unstable structure than wollastonite ceramics and thus, it is more reactive. The silicon dissolved from the bioactive systems may be adsorbed on the surface of the substrates, as $Si^{4+}$, acting as a nucleating agent [20]. The behavior of pH with time for the SBF corresponding to the samples treated with no bioactive system indicates that the increase of pH is not only due to the ionic exchange between the bioactive system (wollastonite or bioactive glass) and the SBF, but also, other reactions, as the formation of Zr-OH groups on the ceramic substrates, may be involved.

The most important factors on the apatite formation on the zirconia/alumina composite studied are, firstly, the re-immersion method and secondly, the presence of wollastonite during the immersion in SBF.

A thinner layer, with a morphology consisting of smaller ceramic agglomerates was obtained using bioactive glass,. The calcium content in bioactive glass is lower than that in wollastonite. This can explain the difference between the characteristics of the apatite layers obtained using bioactive glass and wollastonite. However, better results were obtained using the re-immersion method without a bed of bioactive system, than using a bed of bioactive glass. Further research needs to be performed, but the behavior observed using bioactive glass may be due to the following: as indicated by the pH behavior with time of immersion, the bioactive glass is highly reactive, which leads to the formation of apatite on its own surface at a high rate. Thus, the release of $Si^{+4}$ and $Ca^{+2}$ from the bioactive glass into the SBF decreases with time of immersion. Then, the only sources of $Ca^{+2}$ are the SBF and the 1.4 SBF and these ions may be involved in forming the apatite layer, mainly on the highly reactive material, as on the bioactive glass. Thus, a thinner layer is observed on the bioinert substrate. Furthermore, the presence of a higher content of other elements in the simulated body fluids due to the partial dissolution of the bioactive glass may decrease the nucleation rate of apatite on the substrate.

## 5 Conclusions

Bioactive zirconia/alumina composites were obtained using a biomimetic method consisting in the immersion of the samples in SBF for 7 days, followed by the immersion in 1.4 SBF for 14 days. An apatite layer was observed on the biomimetically-treated samples without and with a bed of bioactive systems. A dense and thicker bone-like apatite layer was formed on the ceramic composite using a bed of wollastonite during the first seven days of immersion. The thickness of this layer was approximately of 30 $\mu$m. When no bioactive system was used during the immersion period of the composite in SBF, a homogeneous bone-like apatite layer was also formed. The thickness of this layer was about 20 $\mu$m. On the other hand, using bioactive glass, the morphology of the layer consisted of smaller ceramic agglomerates and the topography was highly irregular. The thickness of this layer was close to 15 $\mu$m.

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## References


1. C. PICONI and G. MACCAURO, *Biomaterials* **20** (1999) 1.
2. L. L. HENCH and J. WILSON, in "An introduction to bioceramics", edited by L. L. Hench and J. Wilson. (World Scientific Publishing, London 1993) p 1.
3. R. STEVENS, in "Engineered materials handbook: ceramics and glasses" (ASM International, EUA, 1991) p. 775.
4. J. L. DRUMMOND, *J. Am. Ceram. Soc.* **75** (1992) 1278.
5. K. SHIMIZU, M. OKA, P. KUMAR, Y. KOTOURA, T. YAMAMURO, K. MAKINOUCHI and T. NAKAMURA, *J. Biomed. Mater. Res.* **27** (1993) 729.
6. D. J. KIM, M. H. LEE, D. Y. LEE and J. S. HAN, *J. Biomed. Mater. Res.* (Appl Biomater) **53** (2000) 438.
7. M. NAWA, N. BAMBA, T. SEKINO and K. NIIHARA, *Ceram.Int.* **24** (1998) 497.
8. T. KOKUBO, *J. Ceram. Soc. Jpn.* **99** (1991) 965.
9. D. A. CORTES, A. A. NOGIWA, J. M. ALMANZA and S. ORTEGA, *Mater. Lett.* **59/11** (2005) 1352–1355.
10. T. KOKUBO, F. MIYAJI, H. M. KIM and T. NAKAMURA, *J. Am. Ceram. Soc.* **79** (1996) 1127.
11. T. KOKUBO, H. KUSHITANI and S. SAKKA, *J. Biomed. Mater. Res.* **24** (1990) 721.
12. L. L. HENCH, *J. Am. Ceram. Soc.* **74** (7) (1991) 1487.
13. M. UCHIDA, H. M. KIM, T. KOKUBO, M. NAWA, T. ASANO, K. TANAKA and T. NAKAMURA, *J. Biomed. Mater. Res.* **60** (2002) 277.
14. E. JALLOT, *Appl. Surf. Sci.* **211** (2003) 89.
15. Y. LENG, R. XIN and J. CHEN, *Key. Eng. Mater.* **284–286** (2005) 11.
16. D. EICHERT, C. COMBES, C. DROUET and C. REY, *Key. Eng. Mater.* **284–286** (2005) 3.
17. K. HATA, T. KOKUBO, T. NAKAMURA and T. YAMAMURO, *J. Am. Ceram. Soc.* **78** (1995) 1049.
18. P. SEPULVEDA, J.R. JONES and L.L. HENCH, *J. Biomed. Mater. Res.* **61** (2002) 301.
19. P.N. DE AZA, F. GUITIAN, A. MELOS, E. LORA-TAMAYO and S. DE AZA, *J. Mater. Sci.: Mater. Med.* **7** (1996) 399.
20. Y. ABE and T. KOKUBO, *J. Mater. Sci.: Mater. Med.* **1** (1990) 233.