Evaluation of the Apatite Coating on Silicon Nitride Based Ceramics Sintered With RE_2O_3 Additives (RE = Y, La, Yb)

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Abstract. As alternative for alumina and zirconia implants, silicon nitride based ceramics are considered promising candidate due to its biocompatibility and mechanical properties. However, this materials exhibit a bioinert character, leading to clinical failures. To overcome this problem, a biomimetic coating of hydroxyapatite is proposed in this paper, so that the surface can be bioactive and, consequently, the osteointegration process can be enhanced. Silicon nitride samples were sintered with different additives (Y, La and Yb) and the surfaces before and after coating were characterized by diffuse reflectance infrared Fourier transformed (DRIFT), X ray diffraction (XRD) and scanning electron microscopy (SEM). The results showed that the surfaces of bioinert silicon nitride samples sintered with different additives could be transformed into bioactive by the formation of a hydroxyapatite layer through biomimetic process.

Introduction

Alumina (Al_2O_3) was the first ceramic applied as biomaterial for total joint replacement. Despite the excellent biocompatibility, the low fracture toughness of such material can induce to brittle fractures. Zirconia (ZrO_2) was considered an alternative biomaterial, but have the disadvantage of high degradation rate in biological medium [1,2]. To overcome these limitations, other structural ceramics have been researched and proposed as bioinert materials, such as silicon carbide (SiC) [3,4] and silicon nitride (Si_3N_4) [5,6].

Si_3N_4 based ceramics have been used as structural materials in a wide range of applications due to their high hardness, high heat resistance, high fracture toughness and excellent wear resistance. The structural applications include heat exchangers, turbine and automotive engine components, valves and cam roller followers for gasoline and diesel engines, wear surfaces, etc [7,8,9]. As biomaterial, Si_3N_4 is promising due to its non-cytotoxic behavior [10]. Nowadays, total hip arthroplastic bearings have been successfully manufactured from Si_3N_4 powders [11].

It is known that additives are required to promote densification of Si_3N_4 ceramics due to Si-N covalent bond and the low diffusion coefficient [12]. These additives are in general oxides, such as alumina, yttria, magnesia and rare earth oxides [13] that react with the silica layer on the Si_3N_4 powder surfaces to form a liquid phase. Liquid phase sintering involves α-Si_3N_4 particle rearrangement, dissolution of the α-phase, diffusion of Si and N atoms and precipitation of the β-phase [14], followed by grain growth [15].

The type and total amount of additives used can be adjusted to optimize the process and to increase the desired properties of the final Si_3N_4-based ceramics, depending on the application. These modifications render controlled microstructures that are composed of elongated grains.

Because most rare earth additives do not form a solid solution with Si_3N_4, the liquid phase, after cooling, forms at grain boundaries as an amorphous or partially crystalline phases [16]. In other words, the Si_3N_4 grains are surrounded by an intergranular glass or an intergranular film containing the rare earth element [1].

The main characteristic of a bioinert material, including all metals and oxides/covalent ceramics (such as Al_2O_3, ZrO_2, SiC and Si_3N_4) is the formation of a fibrous capsule surrounding the implant, so that the absence of chemical bonds with the living tissues at the implant/tissue interface can lead to clinical failures of an implant [1].

In order to associate the high mechanical properties of a bioinert material with the bioactivity of calcium phosphate phases, different strategies are proposed in literature, such as substrate coatings with a bioactive layer of calcium phosphate [17,18,19]. For the last one, several methods can be applied, such as plasma spraying, electrodeposition [20], sputter deposition [21] sol-gel [22] and biomimetic coating [23,24,25]. By this method, a bone-like apatite surface layer can be produced in an acellular simulated body fluid (SBF) with ions composition similar to that of inorganic part of human blood plasma [26]. Two steps are involved in the process: i) nucleation and ii) precipitation and growth of the apatite layer. The first step occurs during the immersion of the ceramic surface into a synthetic solution simulating the blood plasma, i.e., into the simulated body fluid (SBF), containing a nucleant agent. The second step is consequence of a subsequent immersion of the ceramic surface into a concentrated simulated body fluid (1.5 SBF) [24]. The nucleant agent in the conventional biomimetic method is a bioglass, but there is another biomimetic method in which the nucleant agent is a sodium silicate solution [21].

This paper describes a alternative methodology to produce bioactive coatings on the surface of ceramic by biomimetic method using sodium silicate solution (SS) with nucleating agent. Prior to immersion in 1.5 SBF, the ceramic is subjected to soaking in sodium silicate solution (SS). This treatment creates several calcium phosphate precursor sites over the surface, which will eventually create favorable condition for the nucleation and growth of HAp. This procedure is adopted so that the reactions could happen as follows: i) adsorption of silicates ions of the solution on the ceramic surface; ii) nucleation of hydroxyapatite on the adsorbed ions and iii) growth of the hydroxyapatite nuclei and growth of the thickness of the layer [23]. Previous works performed with different substrates showed the used concentration of sodium silicate is adequate to promote a hydroxyapatite layer at the end of the coating process [23, 25].

The biomimetic coating process was successfully developed as a surface treatment of Si_3N_4 substrates [27]. With this experimental methodology, it was possible to obtain a bulk bioceramic with excellent mechanical properties with its bioactive surface i.e., coated with an calcium phosphate phase similar to bone tissue composition, so that chemical bonds are formed at interface and, consequently, the osteointegration process can be improved.

With this highlights, the objective of this study is to compare the influence of Y, La and Yb oxides additives on the bioactive surface characteristic of silicon nitride substrates. The experimental procedure was carried out with the biomimetic method with a sodium silicate solution as nucleant agent.

Experimental Procedure

Samples preparation

Silicon nitride powders (Si_3N_4, grade M11, Hermann C. Starck, Germany) were mixed with 4.5 wt% alumina (Al_2O_3, A-16 SG, Alcoa) and 4.5 wt% of high purity (> 99.9%) commercial powders as additives (Y_2O_3 (Hermann C. Starck, Germany), La_2O_3 (Sigma Aldrich, USA), Yb_2O_3 (Sigma–Aldrich, USA)). The pellets (SN-Y, SN-La and SN-Yb according to different additive) were obtained through conventional uniaxial (20 MPa) and cold isostatic pressing (200 MPa) of the powders. Sintering was carried out at 1750ºC/1h (Astro 1000, 4560, FP 20, Thermal Technology Inc.) with graphite heating elements and a nitrogen atmosphere. The microestrutural and mechanical

analysis were performed in previous studies [28]. Before coating, all samples were rectified using a diamond-encrusted drill (D-91, Winter).

Coating by the biomimetic method

a) Soaking samples. Rectified sintered samples were coated with apatite using the biomimetic method, as described by our earlier work [27].

Briefly described, samples were exposed to sodium silicate solution at 37 °C for seven days. After the incubation period, the samples were washed in deionized water and dried at room temperature, so that they could be immersed into 1.5 SBF. The samples were soaked in 1.5 SBF for seven days at 37 °C and the solution was changed every two days. At the end of this period, the procedure of washing and drying of the samples was carried out. The immersion of both sodium silicate and 1.5 SBF solutions was done in polipropylene frasks using a shaker at 40 rpm at 36.5°C (TE-420, Tecnal).

b) Characterization. After coating, the surface samples were characterized by diffuse reflectance infrared Fourier transformed (DRIFT, Thermo Nicolet, Nexus 400), X ray diffraction (Siemens D 5000), scanning electron microscopy (Philips, XL30) with energy dispersive spectroscopy (LEO-440I / Oxford).

Results and discussion

Table 1 summarizes the densities and roughness of Si_3N_4 samples sintered with different additives. The final densities were between 94 and 98.5% of the theoretical density (td), which are dependent on the additive used. As observed in our previous work [28], the density values tend to increase with increasing ionic radius of the rare earth. As a result, the SN-La sample (with 98.5% td) had the highest density and the SN-Yb sample (with 94% td), the lowest. After rectified process, SN-La samples showed higher roughness as compared with SN-Y and SN-Yb.

The DRIFT spectrum of studied samples (Fig. 1) revealed the presence of several functional groups on surface. After rectified process, (Fig. 1a), Si-O and Si-N bonds vibrations of the Si_3N_4 [29,30] were identified for all samples, at 590, 1025, 1202 cm $^{-1}$. After coating (Fig. 1b), strong bands of PO_4^{-3} (585, 1010 and 1100 cm $^{-1}$) and weak bands of CO_3^{-2} vibrations (868 and 1485 cm $^{-1}$) can be identified. Moreover, typical bands of H_2O (1647 cm^{-1}) and OH^- (between 3000 and 3600 cm^{-1}) can also be noticed for all samples. The additives used to sinter Si_3N_4 samples seem to not interfere on the functional groups bands position. These results indicate the apatite formation on Si_3N_4 surfaces after treatment with the biomimetic method. The apatite nucleation on silicon nitride surface can be attributed to the formation of Si-OH bonds on the Si_3N_4 surface by the adsorption of the SS solution ions, and consequently the hydration of the silica layer on the surface of Si_3N_4. After the formation of apatite nuclei, they could grow by the immersion into 1.5 SBF.

Table 1: Density and roughness of the silicon nitride-based ceramic samples

Sample identification	Theoretical density (g/cm^3)	Density (%td)	Roughness (μm)
SN-Y	3.25	95.0 ± 1.2	0.65 ± 0.05
SN-La	3.28	98.4 ± 0.4	0.77 ± 0.03
SN-Yb	3.30	94.1 ± 0.5	0.65 ± 0.12

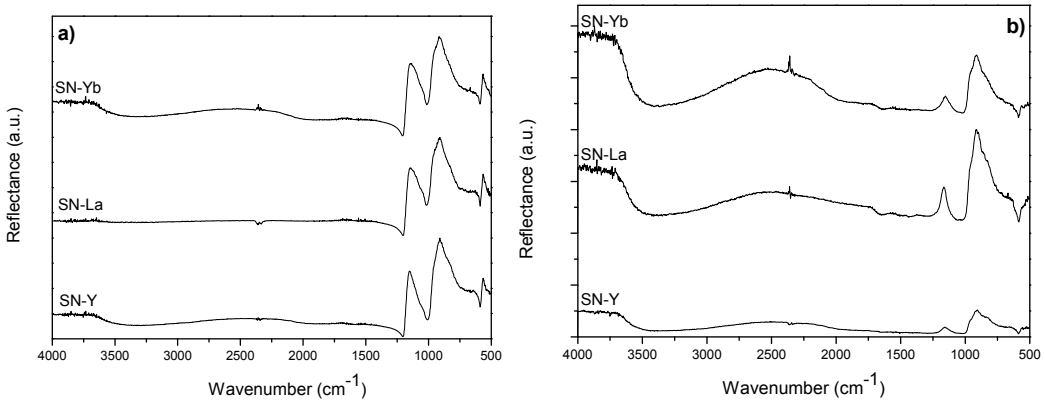

Fig 1: DRIFT spectra of SN samples surface: a) before coating; b) after coating

Before coating, the X-ray diffraction patterns of the Si_3N_4 samples (Fig. 2a) reveal only the β-Si_3N_4 phase (JCPDS 33-1160), indicating dissolution of the α-Si_3N_4 phase and re-precipitation of the β-Si_3N_4 phase during sintering, as a typical behavior in liquid phase sintering mechanisms. Secondary crystalline phases did not form during cooling, indicating that the secondary phase is amorphous in the grain boundary regions. After coating (Fig. 2b), besides β-Si_3N_4 phase, it can be observed broad peaks of hydroxyapatite (JCPDS 09-432) for all samples, confirming that the layer obtained on the silicon nitride surfaces, after the treatment with the biomimetic method, is predominantly formed by hidroxycarbonate apatite (HCA). Moreover, for SN-Y samples, $Mg_2P_2O_7$ and NaCl crystalline phases were also identified. For the other samples, these phases can be present, although lower than the limit detection technique.

Before coating, the scanning electron micrographs of rectified surfaces of sintered Si_3N_4 with different additives showed a similar overall microstructure of all ceramics (Fig. 3, left size). The surfaces were mostly irregular and rough. All samples presented grooves with different deepness due to the rectification process. The SN-La sample (Fig. 3b) presented microstructure which confirms higher roughness and density as compared to another samples.

After coating, a HAp layer can be seen for all samples, precipitated preferred on rectified deep profiles (Fig. 3, right size). This result indicates that roughness should be presented on surface material, to induce HAp precipitation. The morphology of the layer formed on Si_3N_4 surfaces sintered with different additives is very similar to that of the coatings obtained on titanium and titanium-alloys surfaces when the biomimetic method is used [31]. Comparing Si_3N_4 samples, it can be seen that SN-Y (Fig. 3e) showed lower amount of HAp due to higher density as compared with others samples, as well as other concurrent phases. The chemical analysis of the layer formed on the Si_3N_4 surface, obtained by energy dispersion spectroscopy (Fig. 3, right side, top of each sample) show the presence of Ca, P, Mg, Na, Cl, Si, O, K, Al and C ions in all coated samples. Moreover Y, La and Yb were identified in SN-Y, SN-La and SN-Yb samples,

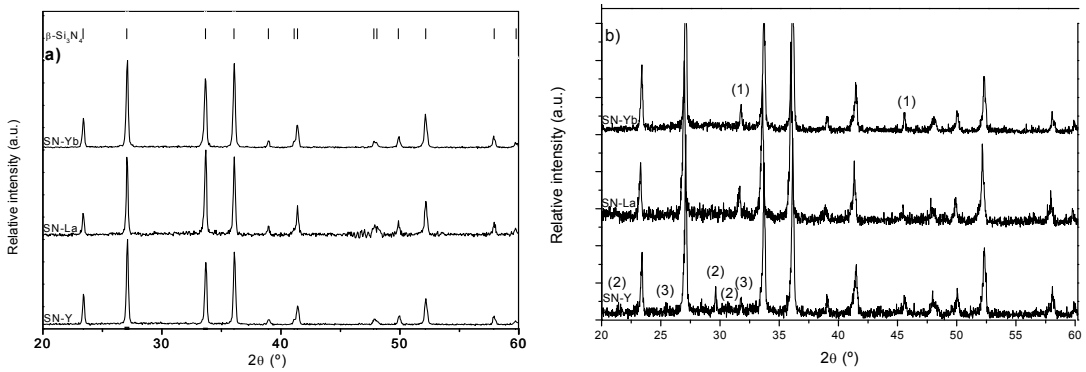

Fig. 2: X-ray diffraction (XRD) spectra for Si_3N_4 samples: a) before coating; b) after coating
(1): HAp (JCPDS 09-0432); (2): $Mg_2P_2O_7$ (JCPDS 05-0582); (3): NaCl (JCPDS 05-0628)

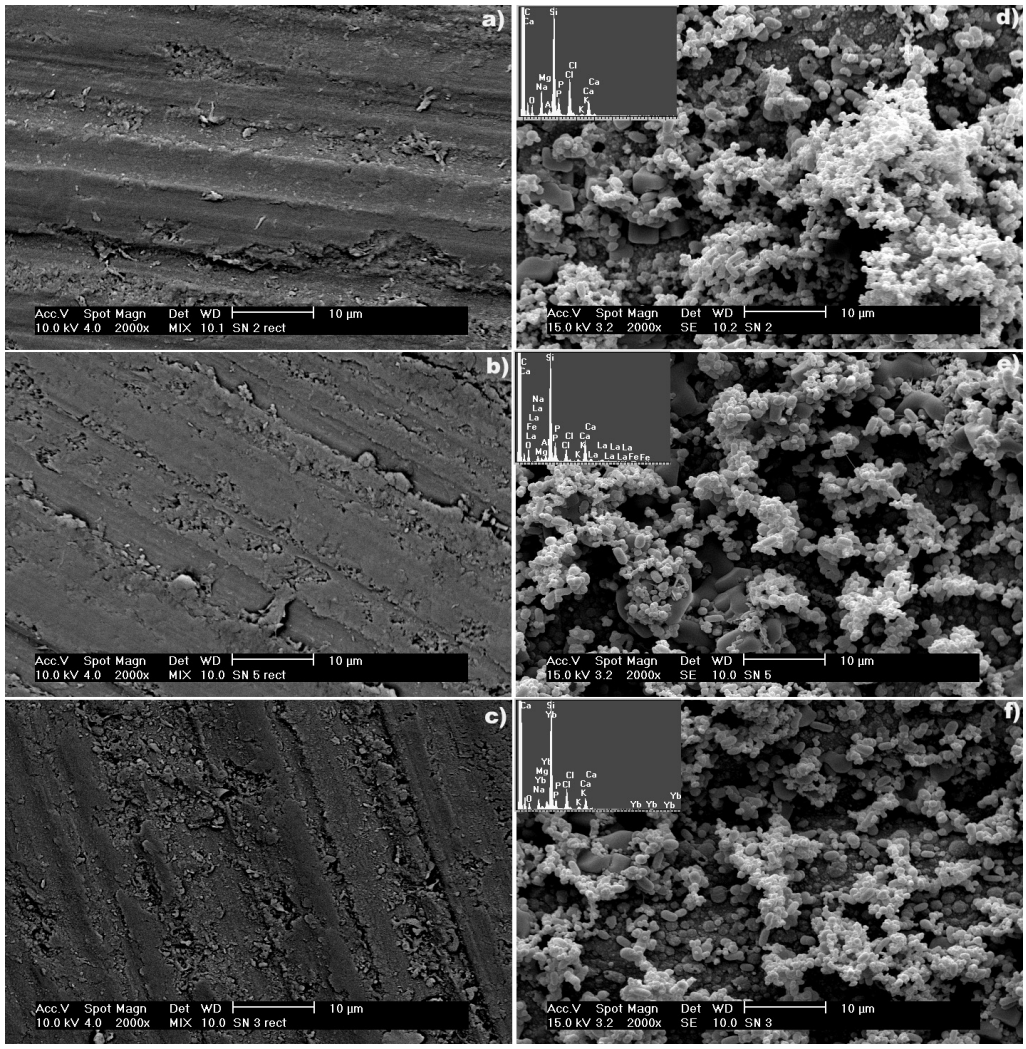

Fig. 3: Scanning electron micrograph (SEM) of the Si_3N_4 surface. Left side: before coating; right side: after coating; a) and d): SN-Y; b) and e): SN-La; c) and f): SN-Yb

respectively, according to the additive used. These results confirm the presence of PO_4^{3-} and CO_3^{2-} groups identified by DRIFT (Figure 2) and leading the formation of HCA. These results indicated the affinity of the precipitates with Si_3N_4 based ceramic, suggesting that this material has adequate superficial features to become bioactive.

Summary

The biomimetic method was suitable to promote the bioactivity of an inert surface through the deposition of a dense layer of hydroxyapatite on silicon nitride surfaces. With this process, a biomaterial with high mechanical properties, associated with excellent interaction with the living tissues can be successfully developed. Comparing additives, Y, La and Yb seem to have the same effect in the bioactive behavior of silicon nitride surfaces ceramics, since it was observed no difference in regard the microstructural analysis. Certain roughness should be present on surface samples to induce the bioactive process.

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