SiO_2-CaO Vitreous Films Deposited onto Ti6Al4V Substrates

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A sol-gel dipping method has been utilised to deposit SiO_2-CaO films onto Ti6Al4V alloy substrates. These layers were prepared by the dip-coating technique from a series of precursor solutions with different concentrations of glassy $xSiO_2$-$(1 - x)$CaO ($x = 0.8$ mol) diluted with absolute ethanol. The characterisation of the films by a variety of techniques reveals differences in the textural properties and in the films' thicknesses depending on the sol concentration in the precursor solution. Concentrated precursor solutions yield porous layers with a higher thickness and surface roughness than those obtained from the dilute ones.

Introduction

Titanium and its alloys are widely used in the aerospace, chemical and sporting equipment industries. It was not until the 1960s, however, that Ti6Al4V alloy began to be used as a surgical implant material because of its excellent mechanical properties (tensile strength of 860 MPa and yield strength of 790 MPa), and its lightness (specific gravity of 4.5 g/cm^3). Ti-based alloys are not the best from a biological point of view, however, since they corrode away when implanted; this disadvantage led to the discontinuation of the use of Ti6Al4V alloys for load-bearing applications.[1,2] It is commonly believed that this is due to their poor tribomechanical properties under certain physiological conditions, which could cause a local build-up of low pH acidity and high Cl^- ion concentration.

An interesting alternative for protection of metal surfaces against corrosion phenomena is to employ ceramic coatings. Several attempts have been made in this sense, using sophisticated deposition techniques such as PVD and CVD, ion implantation, reaction-assisted and laser coating.[3−5]

The dipping method is a much simpler, versatile and cost effective option which, combined with the sol-gel chemical method, allows the coating of metal surfaces with ceramic layers. The quality of these coatings is strongly determined by the chemical synthesis of the starting sols. In this initial stage, the control of viscosity, ageing and/or solvent allows the determination, at least indirectly, of the roughness, the porosity and thickness of the deposited ceramic layer.[6,7]

Using this method, layers of hydroxyapatite have been deposited onto metallic substrates of the Ti6Al4V alloy.[8] As an alternative solution to the deposition of hydroxyapatite onto titanium alloys, the deposition of bioactive glasses yields an additional advantage: besides its role as a barrier against corrosion, it could improve the bonding with tissues by means of a bioactive interphase.

The aim of this work is to deposit glassy coatings onto Ti6Al4V alloy. The glass chosen for this type of coating is SiO_2-CaO, which our group produces in bulk forms[9,10] and

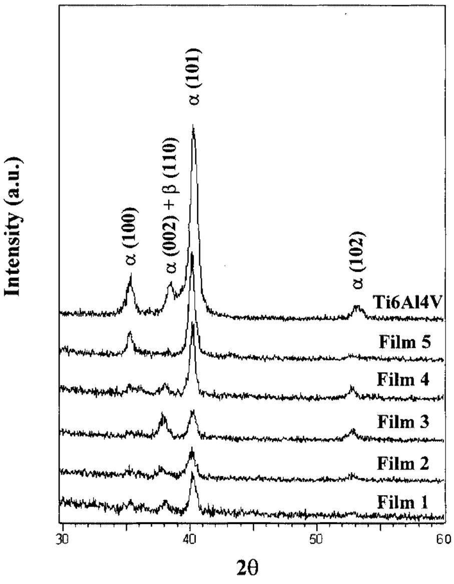

Figure 1. XRD patterns of the Ti6Al4V wafers before and after coating with the different precursor solutions

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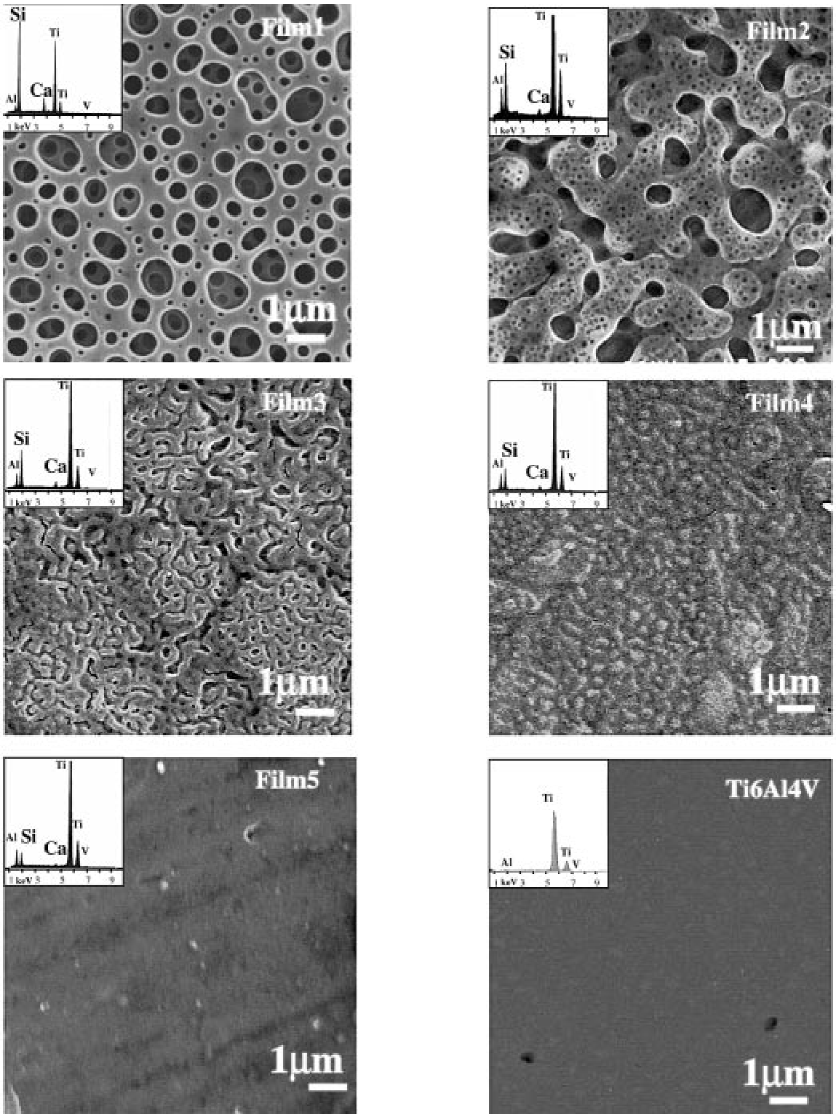

Figure 2. SEM micrographs and EDS spectra of the coatings obtained from the different precursor solutions

where in vitro and in vivo studies have confirmed the bioactivity of such a composition. The films are characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray dispersive energy spectroscopy (EDS), reflection ellipsometry and scanning force microscopy (SFM).

It is our purpose to define the production method for these coatings. Their potential applications go beyond the clinical field, and therefore special care is devoted to the control of thickness, roughness and porosity of the deposited layer, through the synthesis conditions, in order to tailor those parameters to the specific application proposed.

Results and Discussion

Five SiO_2-CaO vitreous films were deposited onto Ti6-Al4V substrates by the dip-coating method from a series of precursor solutions with different concentrations of glassy $x SiO_2$-$(1-x)$CaO ($x = 0.8$ mol) diluted with absolute ethanol. The X-ray diffraction patterns show, for all the synthesised films, a broad peak between $15 < 2\theta < 30°$ that could correspond to amorphous silica. Sharp peaks that correspond to the substrate are only observed for 2θ values between 35.1 and 53.0. Figure 1 shows that the intensity of these diffraction maxima decreases as the ethanol volume used in the sol preparation decreases.

SEM, SFM and reflection ellipsometry observations manifest the differences in the textural properties, which depend on to the solution used for coating.

Figure 2 shows the SEM micrographs and EDS spectra of the coatings obtained from the different precursor solutions and the substrate. Film 1 (obtained from the 1:2 sol) presents large pores of different sizes. The pore size ranges between 150 ± 50 nm and 875 ± 50 nm. In film 2 (from the 1:4 sol) the number of pores with a 150 ± 50 nm diameter with regard to those of 875 ± 50 nm is higher than in film 1. The micrograph corresponding to film 3 (1:6 sol) shows a film with a noticeably different structure, consisting of crossed grains. Furthermore, the films 4 (1:8 sol) and 5 (1:12) present a rough structure. Consequently, when the precursor solution has a low ethanol content (films 1 and 2) the films are porous, while as ethanol volume rises the films become more compact (films 3, 4 and 5).

The EDS analyses of the surfaces show that Si and Ca are present in the coatings, while Ti, Al and V, constituents of the substrate, can also be detected. Differences between the relative intensities of substrate (Ti, Al, V) and deposited elements (Ca, Si) are observed. The higher the alcohol content in the precursor solution, the higher the intensity of Ti, Al, V. The Si and Ca content measured by EDS in all cases are 81.2 and 18.8 atom %. These elements have been found homogeneously distributed throughout every sample. These results indicate that the composition does not depend on the sol concentration.

In Figure 3, thickness and refraction indexes of the films obtained by reflection ellipsometry are plotted as a function of the precursor solution concentration. Thickness, ranging from 240 to 1639 nm, decreases as the alcohol content increases as can be expected since the amount of sol drawn also lessens. These data are corroborated by the intensity of the diffraction peaks and EDS observations (see Figure 1 and inset in Figure 2). The refraction index, on the other

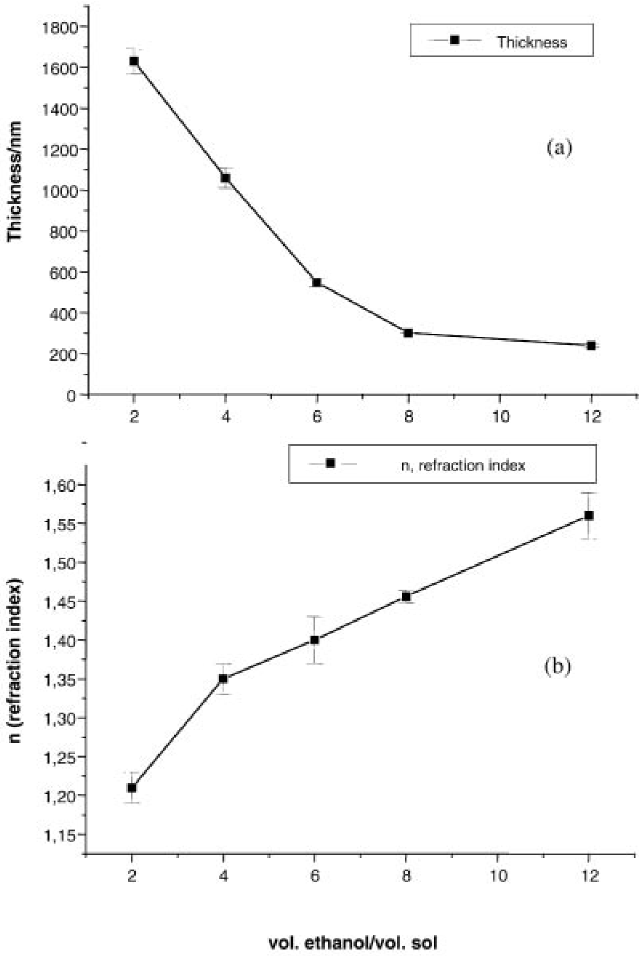

Figure 3. (a) Thickness and (b) refraction index of the films as function of the concentration of the precursor solutions

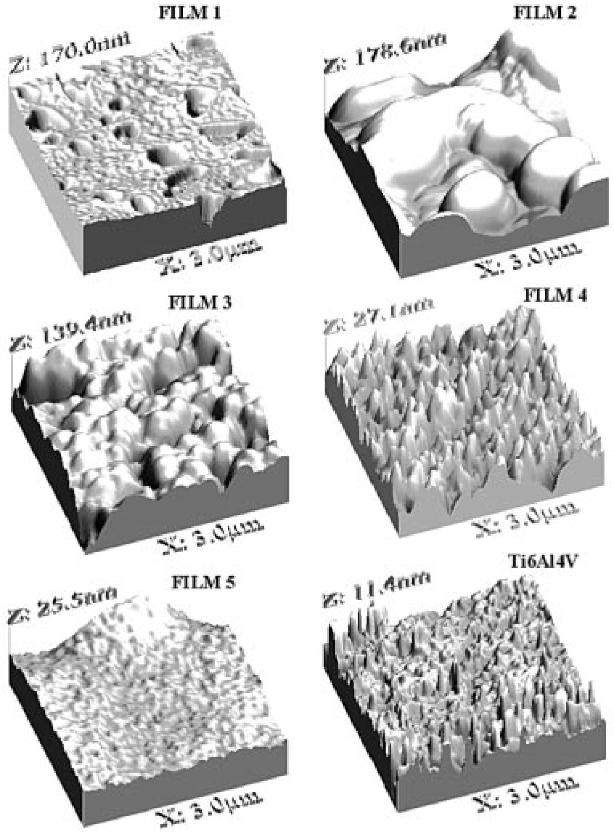

Figure 4. SFM images of the substrate and films; image size: 3 μm × 3 μm

Table 1. Nomenclature, porosity, roughness and grain size of the films obtained

Nomenclature	Precursor solutions (Vol sol:Vol Ethanol)	% Porosity $\rho = (n^2 - n_p^2)/(n^2 - 1)$	Roughness (nm)	Grain size (nm)
Film 1	Sol 1:2	65.6 ± 3.0	25	–
Film 2	Sol 1:4	42.6 ± 3.4	36	800
Film 3	Sol 1:6	34.4 ± 5.3	26	400
Film 4	Sol 1:8	26.2 ± 1.5	6	190
Film 5	Sol 1:12	9.8 ± 6.0	2	90

hand, increases as the precursor concentration decreases. The refraction index, on the other hand, increases as the precursor concentration increases: 1.21 and 1.55 for films 1 and 5, respectively. These results agree with the diminished porosity observed by SEM because the refraction index (n) is related to porosity by the equation shown in the Exp. Sect. Accordingly, n increases as the porosity decreases (see Table 1).

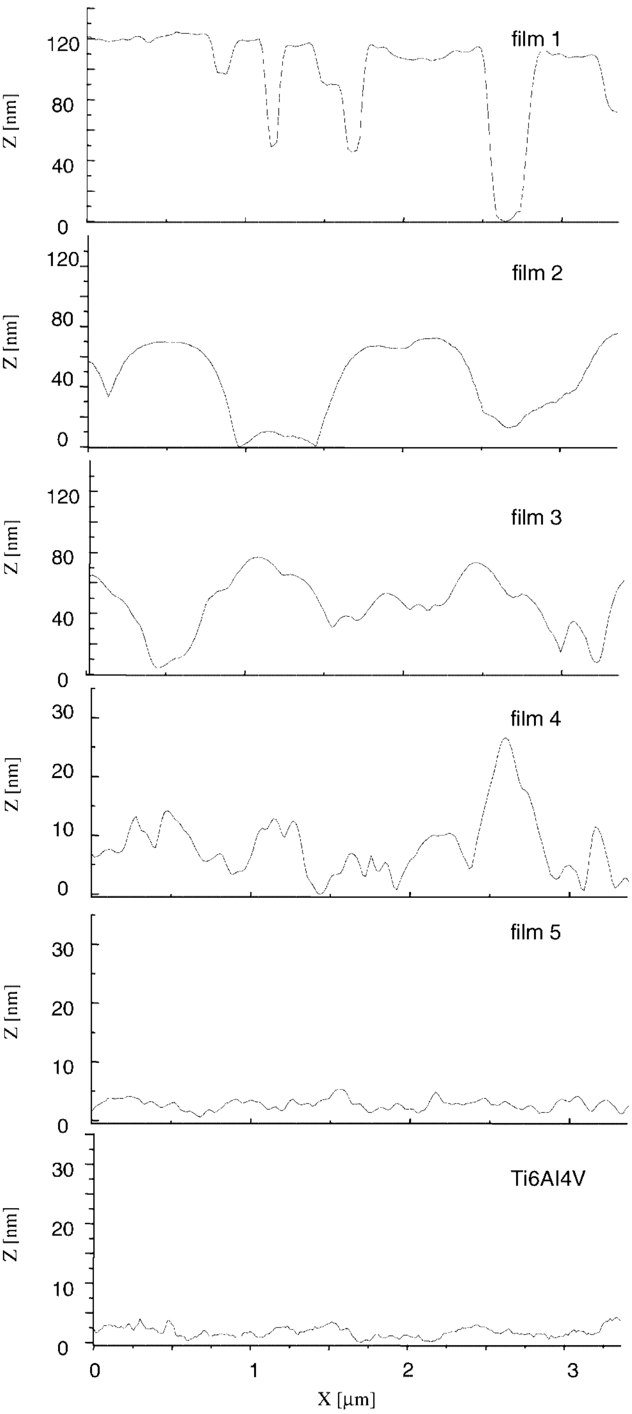

Figure 5. Profiles obtained from the SFM images performed in the different films; note that the profiles corresponding to films 1, 2 and 3 have the same scale, and that the profiles corresponding to films 4, 5 and substrate are presented at a higher magnification

The SFM images shown in Figure 4 are in agreement with the SEM images presented in Figure 2. The advantages in the use of SFM lie in the real 3D information offered, which allows us to study the evolution of the surface roughness versus the precursor concentration. In particular, the roughness (rms) values have been calculated for the different films. The rms values range from 2 nm to 25 nm as shown in Table 1. The lower roughness corresponds to film 5 and an increase of the rms value is observed when the precursor concentration increases. The evolution of the film structure can also be deduced from the analysis of the profiles in Figure 5 obtained from the SFM data. In addition, the SFM images show the increase of the grain size as the precursor concentration increases (see Table 1). Moreover, we have found that, for a precursor concentration of 1:4, the grains start to coalesce, giving an almost continuous film for 1:2 precursor concentrations.

It should also be noted that the structure as well as the roughness of the thicker film, shown in Figure 6, differ from those observed on the other films. This almost continuous film 1 has pores with discrete depth values of 20 nm, 40 nm, 60 nm, 80 nm and 100 nm.

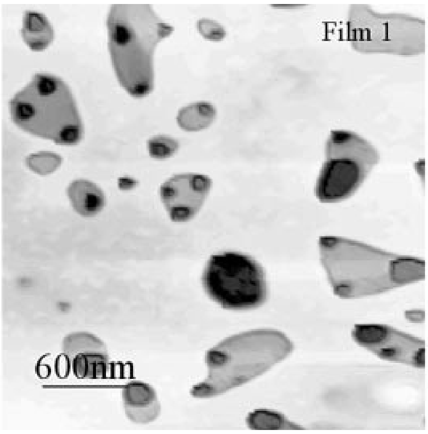

Figure 6. Top view SFM image of film 1; image size: 3 μm × 3 μm

The effect of increasing the alcohol concentration on the sol kinetics is that of slowing down its polymerisation.[6,7,11] Accordingly, the polymerisation of 1:2 sol is faster (and exhibits higher viscosity) than in 1:12 sol. In the latter case, the Si-O-Si aggregates are smaller and easily packed, forming more compact and homogeneous films of lower thickness.

Conclusions

SiO_2-CaO films have been deposited onto Ti6Al4V metal alloy wafers by dip-coating in precursor solutions, a cost-effective and controllable method.

The films are noncrystalline, and are independent of the dipping solution characteristics. In addition, the actual compositions of films do not depend on the precursor solution concentration. However, thickness and texture of surfaces depend on the precursor solution concentration.

The porosity, roughness, grain size and thickness depend on the amount of ethanol present in the dipping solutions. Concentrated dipping solutions yield porous films with higher thickness and surface roughness. Less concentrated precursor solutions produce dense films with higher refraction indexes and lower surface roughness and grain size. The thicker coating shows a continuous film with well-defined pore depths.

In summary, the dip-coating deposition method allows us to tailor the thickness, surface roughness and porosity of the obtained product that can be useful for a variety of applications in the materials science field.

Experimental Section

Dipping Solution Preparation: A SiO_2-CaO, [Si]/[Ca] = 4, sono-sol was elaborated by hydrolysis and polycondensation of tetraethylorthosilane (TEOS) and $Ca(NO_3)_2{\cdot}4H_2O$ under acidic conditions (pH $[HNO_3] = 0.5$) with $R_w = [TEOS]/[H_2O] = 8$. Ultrasound waves of 20 MHz were generated by a sonicator device (Sonic & Materials Vibracell), delivering 15 $W{\cdot}cm^{-3}$ of ultrasound power to this liquid mixture for three minutes.

This sol, diluted with different amounts of alcohol (99.99% purity), was distributed in five different containers to obtain the precursor sols named as follow: 1:2 Sol, 1:4 Sol, 1:6 Sol, 1:8 Sol and 1:12 Sol (the figures indicating the sol to ethanol volumes ratio). The sols were aged for 30 days at room temperature before starting to prepare the films.

Films Preparation: Before film deposition, Ti6Al4V metal wafers, provided by IQL (Industrias Quirúrgicas de Levante S.L., Biomet Merck), 13 mm diameter and 1 mm thick, were polished with SiC of 220, 500, 800 and 1200 grit and then with 3−1 μm diamond paste. Finally, the polished discs were washed for 5 min in an ultrasound bath distilled water, alcohol and acetone.

The coating procedure was carried out in a device which allows the control of the substrate extraction at a rate between 50 and 2550 μm/s. Metal substrates were grasped by dipping tweezers, dipped into one of the previously prepared solutions, and then taken out at a constant speed of 1500 μm/s. After muffling the pieces with a thin cloak of sol, they were dried in air at room temperature for 10 minutes and afterwards in an oven at 100 °C for 20 minutes. The samples were stabilised at 550 °C for 10 minutes. This process was repeated six times. Finally, the wafers were washed in an ultrasound bath for five minutes.

Film Characterisation: The resulting films were characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray dispersive energy spectroscopy (EDS), reflection ellipsometry and scanning force microscopy (SFM).

X-ray diffraction experiment were carried out using Cu-K_α radiation ($\lambda = 1.54056$ Å) in an automatic powder diffractometer (Philips X′Pert MPD) with a thin-film attachment. Scanning measurements at grazing incidence were done in the range $10° < 2\theta < 60°$. The fixed incidence angle was 0.5° for all samples.

SEM and EDS observations were performed on a JEOL 6400 microscope equipped with a Pentajet inper ATW system analyser microscope.

The measurements of reflection ellipsometry were carried out with a PLASMOS SD-2300 automatic ellipsometer with a spot size of 2 mm^2 and a wavelength of 632.8 nm. The ellipsometry angles, Ψ and Δ, were obtained at the same point, under multiple incidence angles (MIA), and are correlated with film thickness and reflective index, n, by means of McCrackins routines[12,13] by interactive calculus with software provided by PLASMOS.

The film porosity, ρ, (as shown in Table 1) was estimated from the refraction indexes calculated by Equation (1),[14]

$$\rho \equiv \frac{n^2 - n_p^2}{n^2 - 1} \qquad (1)$$

where n_p is the refraction index of the film measured by reflection ellipsometry and n the refraction index of SiO_2-CaO bulk glass, $n = 1.61$, calculated as the weighted average of the tabulated indexes for SiO_2 and CaO.[15]

The topography of the samples was obtained by using an Autoprobe-CP SFM from Park Scientific Instruments working in contact mode. Cantilevers with a 0.4 N/m force constant and conical tip were used.

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