Journal of Sol-Gel Science and Technology 26, 1179–1182, 2003

The Role of Precursor Concentration on the Characteristics of SiO_2-CaO Films

I. IZQUIERDO-BARBA AND M. VALLET-REGI*
Departamento de Química Inorgánica y Bioinorgánica, Facultad de Farmacia,
Universidad Complutense Madrid, E-28040-Madrid, Spain
vallet@farm.ucm.es

J.M. ROJO
Departamento de Física de Materiales, Facultad de Física, Universidad Complutense Madrid,
E-28040-Madrid, Spain

E. BLANCO AND L. ESQUIVIAS
Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad Cádiz,
E-11510-Puerto Real (Cádiz), Spain

Abstract. Sol-gel films on Titanium Ti6Al4V alloys polished wafer were prepared from sono-sols obtained from tetraethylorthosilicate (TEOS) and hydrated calcium nitrate. Different precursor solutions were used by dilution of the starting mixture in ethanol. The resulting materials were characterised by different techniques: scanning electron microscopy, energy disperses spectroscopy and atomic force microscopy. These studies showed different texture and porosity properties depending on volume proportions of the sol and ethanol. Solutions with lower ethanol content gave a larger pore distribution and roughness.

Keywords: bioactive glasses, atomic force microscopy, sol-gel dipping process

Introduction

Titanium and their alloys have become of widespread use as biomaterials for odontology and traumatology because these materials are biocompatible with living tissues [1]. Particularly, the alloy Ti6Al4V is very common for making hip, knee, and other prosthesis [2]. However, these materials are bioinert and, consequently, the organism creates a layer of fibrous tissue on the surface that isolates them from the biologic environment. In this case, the implant becomes unstable and crack of the neighbour bone occurs by lack of a close union with the bone tissue. Furthermore, some studies reveal release of metal particles to the biologic environment as a source of intoxication of the organism [3].

In order to alleviate these problems, coating these metal prostheses with bioactive materials has been proposed [4]. These films must feature an outstanding adhesion to the metal substrate, excellent behaviour against corrosion from the biologic environment and a tendency to create bonding with the bone. As a result, there will not be metal cation release and, consequently, the prosthesis average life will lengthen. In this way, Ti6Al4V prostheses coated with a hydroxyapatite (HA) layer produced by plasma spray technique have been used for several years [5]. Unfortunately, the high drying temperature required by this coating technique brings about instabilities of the phase so formed and a weak adhesion to the substrate [6]. Coating these

---

*To whom all correspondence should be addressed.

titanium based implants with a bioactive glasses (able to form hydroxycarbonate apatite on their surfaces in vivo) could be an alternative approach as this method would allow a higher titanium implant osteointegration. Sol-gel dipping method is a genuine low temperature process; it is adequate to avoid the aforementioned problems during processing with other techniques such as enamelling or plasma spraying [7, 8]. The sol-gel dipping process produce a homogeneous and pure thin films. The features of this method are high control of composition, thickness and microstructure of the films formed [9].

In a previous work [10], we synthesised $(SiO_2)_{0.80}$ $(CaO)_{0.20}$ non-crystalline layers from gels and studied their bioactivity in vitro. This study confirmed the bioactive nature of this compound that, consequently, turned out to be a potential candidate for coating titanium prostheses. In the present paper we report on the preparation and characterisation of film from gels of the SiO_2-CaO system deposited onto Ti6Al4V titanium metal alloy by dip-coating and on the effect of the precursor concentration on the film properties. Coatings are characterised by Scanning Electron Microscopy (SEM), X-ray Dispersive Energy Spectroscopy (EDS) and Atomic Forces Microscopy (AFM).

Experimental

Dipping Solution Preparation

A SiO_2-CaO, [Si]/[Ca] = 4, sono-sol was prepared by hydrolysis and polycondensation of tetrethylortosilane (TEOS) and $Ca(NO_3)_2 \cdot 4H_2O$ under acidic conditions (pH $[HNO_3] = 0.5$) with $R_w = [TEOS]/[H_2O] = 8$. Then, ultrasounds of 20 MHz, supplied by a sonicator device (*Sonic & Materials Vibracell*), were applied delivering to this liquid mixture 15 $w \cdot cm^{-3}$ of ultrasound power for 3 minutes.

This sol was distributed in containers where they were diluted with different amounts of alcohol of 99.99 purity to obtain the different precursor sols. In this work the solutions employed were: 1:2 Sol, 1:6 Sol, the figures indicating the sol to ethanol volumes ratio. The sols were let ageing for 30 days at room temperature before proceeding to prepare the films.

Films Preparation

Before film deposition, Ti6Al4V metal wafer substrates, provided by IQL (Industrias Quirúrgicas de Levante), 13 mm diameter and 1 mm thick, were polished with SiC of grit 220, 500, 800 and 1200 and 3–1 μm diamond paste and the washed for 5 min in an ultrasound bath of distilled water, alcohol and acetone.

Coatings were carried out by dip-coating by an outfit designed and implemented at the Department of Condensed Matter Physics of Universidad de Cádiz (Spain). Metal substrates were grasped to the dipping piece, next dipped into one of previously prepared solutions, and then taken out at a constant speed of 1500 μm/s. After muffling the pieces with a fine cloak of sol, they were dried in air at room temperature for 10 minutes and afterwards in a oven at 100°C for 20 minutes. This process was repeated for 4 times in order to augment the thickness the film. Finally, the samples were established at 550°C for 10 minutes.

Film Characterisation

The resulting films were characterised by the following techniques: SEM, EDS and AFM. SEM and EDS observations were accomplished in a JEOL 6400 equipped with a Pentajet inper ATW system analyser microscope. The AFM study was carried out in a Autoprobe cp (Park Scientific). In order to minimise the damage to the film, the analysis was performed in non-contact mode.

Results and Discussion

Coating from Dipping in the 1:2 Sol

The micrograph of Fig. 1 shows a porous film formed on the metal substrate after dipping in the 1:2 sol. The film presents pores of sizes distributed in the 200–800 nm range. The EDS analysis (inset in Fig. 1) reveals that the actual [Si]/[Ca] ratio is 5.1. This higher ratio is thought to be due to the more volatile nature of Ca. The porous structure of the film has been studied more in depth by the AFM (Fig. 2) technique. The profile along the dotted line appears also in Fig. 2. We can see again a wide distribution of pore size, some of these pores presenting a diameter slightly below 1 μm accompanied by tiny ones with a diameter of only some tens of nm. Most of the diameters are in the range between 700 and 250 nm. From a statistical study of this topography for a 100 μm^2 surface, the average depth of these pores was found to be 250 nm with a maximum value of 266 nm.

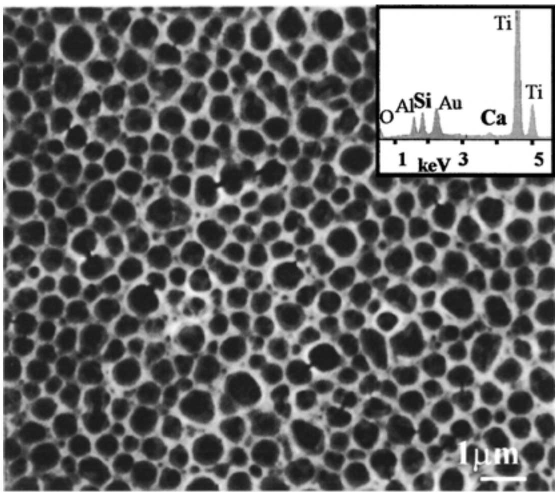

Figure 1. SEM micrograph and EDS pattern of the film on the metal substrate after dipping in the 1:2 sol.

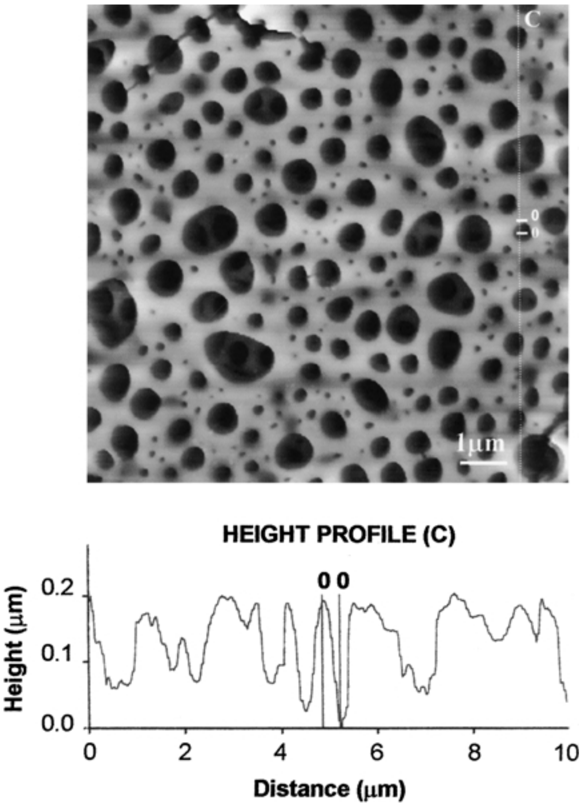

Figure 2. AFM image and two dimensional profiles corresponding to the surface of the film on the metal substrate after dipping in the 1:2 sol.

A surface average roughness (R_{ave}) can be defined by the expression:

$$R_{\text{ave}} = R_{\text{ave}} = \sum_{n=1}^{N} \frac{|Z_n - \bar{Z}|}{N} \tag{1}$$

$\bar{Z}$ being the average height, Z_n the value of height measured at point n and N the number of sampling points. The results of applying Eq. (1) to this sample is 58.2 nm.

Coating from Dipping in the 1:6 Sol

A very homogeneous and dense film is formed after dipping in a more diluted precursor sol (1:6 sol) as can be seen in Fig. 3. The film cracks after few minutes during the observation with the microscope, probably because of the fast elimination of the remaining liquid phase. This outcome permitted clearly to tell the film formed from the substrate as it is verified by EDS. The EDS analysis (Fig. 3) shows that the [Si]/[Ca] ratio is 5.1 also in this sample. The film thickness visualised from the fracture profile seen in Fig. 3 is estimated to be 0.4 μm.

The Fig. 4 is the AFM observation counterpart with the profile registered along the dotted line. The surface is dense and homogeneous. The statistical analysis of a 100 μm^2 area indicates that the average height along this line is 67.4 nm and the average roughness (R_{ave}) is 6.7 nm.

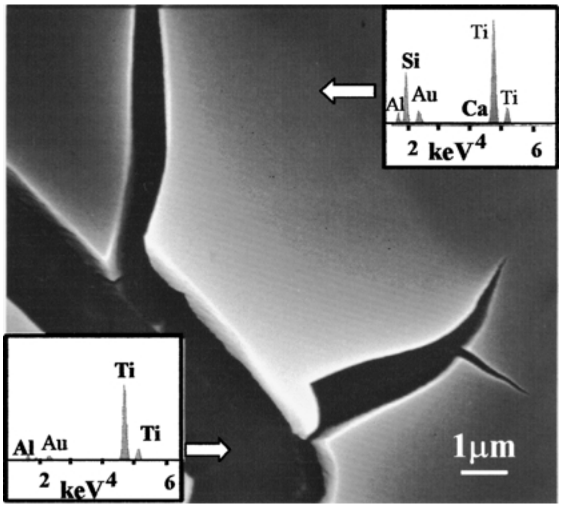

Figure 3. SEM micrograph and EDS pattern of the film on the metal substrate after dipping in the 1:6 sol.

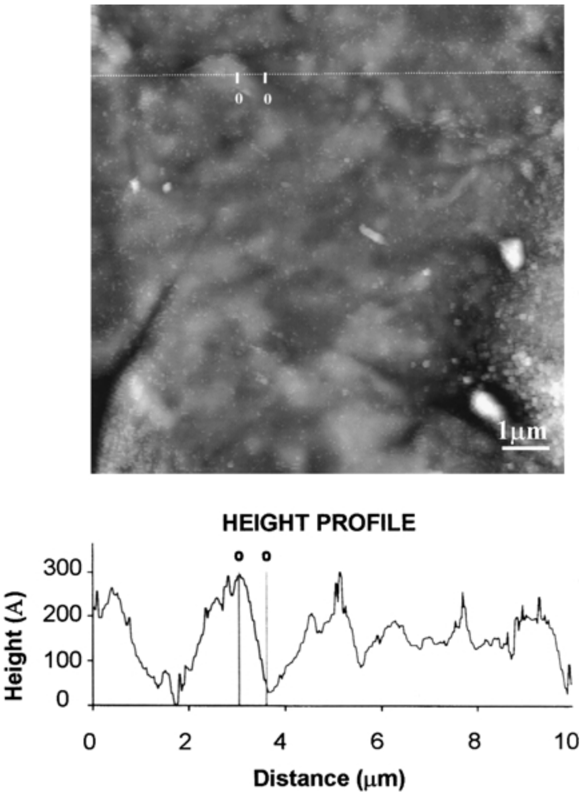

Figure 4. AFM image and two dimensional profiles corresponding to the surface of the film on the metal substrate after dipping in the 1:6 sol.

The effect of increasing the alcohol concentration on the sol kinetics is that of slowing down its polymerisation [11]. Accordingly, the polymerisation of 1:2 sol is more profuse than in 1:6 sol. In the latter case, the Si—O—Si aggregates are smaller and, consequently, easily compact forming dense and homogeneous films.

It is worth pointing out that the general trend of the results presented in this paper are analogous to those obtained by other authors working with SiO_2 [11], TiO_2 and TiO_2-SiO_2 [12].

Conclusions

The main conclusion of the present work is that the textural properties of SiO_2-CaO films formed onto Ti6Al4V substrate can be modified by acting on the sol concentration. The less concentrated is the sol, the denser and smoother is the resulting film. Very concentrated sols produce porous films and, conversely, diluted sols form dense films, the average pore diameter decreasing by an order of magnitude when the alcohol increases. Thus, porosity can be controlled with the precursor sol dilution. During the processing, due to the fact that Ca is more volatile, the nominal ratio [Si]/[Ca] is seen to increase from a nominal value of 4 to a measured value of 5.1.

Acknowledgments

Financial support of CICYT (Spain) trough Research Project MAT.99-0466 is acknowledged. We thank A. Rodríguez and J. González (C.A.I. Electron Microscopy Centre, UCM) for valuable technical and professional assistance. The authors want to express their gratitude to Industrias Quirúrgicas de Levante (I.Q.L) which has facilitated the titanium alloy.

References

1. L.L. Hench, J. Am Ceram. Soc. **74**, 1487 (1991).
2. M. Long and H.J. Rack, Biomaterials **19**, 1621 (1998).
3. K. Meritt, R.W. Margevicius, and S.A. Brown, J. Biomed. Mater Res. **26**, 1503 (1992).
4. K. Yoshida, K. Kamada, K. Sato, R. Hatada, K. Baba, and M. Atsuta, J. Biomed. Mater Res. (appl Biomater) **48**, 778 (1999).
5. K. De Groot, R.G.T. Geesink, C.P.A.T. Klein, and P. Screkoan, J. Biomed. Mater. Res. **21**, 1375 (1987).
6. C.P.A.T. Klein, J.G.C. Wolke, J.M.A. de Blieck-Hogervorst, and K. de Groot, J. Biomed. Mater. Res. **28**, 961, (1994).
7. J.M. Gomez-Vega, E. Saiz, and A.P. Tomsia, J. Biomed. Mater. Res. **46**, 549 (1999).
8. J. Schrooen, H. Van Oosterwyck, J. Vander Sloten, and J.A. Helsen, J. Biomed. Mater. Res. **44**, 243 (1999).
9. C.J. Brinker and G.W. Scherer, *Sol-Gel Science: The Physic and Chemestry of Sol-Gel Processing* (Academic Press, San Diego, 1990), p. 766.
10. I. Izquierdo-Barba, A.J. Salinas, and M. Vallet-Regí, J. Biomed. Mater. Res. **47**, 243 (1999).
11. C.J. Brinker and G.W. Scherer, *Sol-Gel Science: The Physic and Chemestry of Sol-Gel Processing* (Academic Press, San Diego, 1990), p. 143.
12. T. Peltola, M. JoKinen, H. Rahiala, M. Pätsi, J. Heikkilä, I. Kangasniemi, and A. Yli-Urpo. J. Biomed. Mater. Res. **51**, 200 (2000).