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PROCESSING OF FLUORAPATITE SURFACE LAYER ON

ZIRCONIA TAPES BY DIP COATING

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ABSTRACT

Thin fluorapatite (FA) layers on 3 mol% yttria-partially stabilized zirconia (Y-PSZ) substrates have been fabricated by dipping porous zirconia tapes into aqueous 27.4 vol.% fluorapatite slurries. Porous Y-PSZ tapes with 31.4 vol.% porosity were developed using starch and an acrylic latex as fugitive additive and binder, respectively. For comparison, Y-PSZ tapes with 12.7 vol.% porosity were fabricated without starch. The influence of the porous structure of the tape surfaces, top and bottom, on the casting rate and consequently on the layer thickness formed on each surface was studied. Layers formed on the top surface were found to be about 55 and 32 % thicker than those formed on the bottom surface for the tapes fabricated with and without starch, respectively. This difference was attributed to a greater porosity of the top surface with respect to that of the bottom one and was more pronounced for the tapes prepared with starch.

Keywords: porous ZrO₂ tapes, fluorapatite layer, dip coating.

1. INTRODUCTION

Calcium orthophosphates such as fluorapatite $(Ca_{10}(PO_4)_6F_2)$ are widely used as bone substitute materials due to their chemical similarity to the mineral component of mammalian bones and theeth (1). Fluorapatite is non-toxic, biocompatible, not recognized as foreign material in the body and, most importantly, exhibits bioactive behaviour and integrates into living tissue by the same processes active in remodelling healthy bone. Even so, the major limitations to use fluorapatite as loadbearing biomaterials is its mechanical properties, it is brittle with a poor fatigue resistance. The poor mechanical behaviour is even more evident for highly porous ceramics and scaffolds; that is why, in biomedical applications fluorapatite is used primarily as fillers and coatings. Bioinert ceramic such as porous ZrO₂ can be coated with FA to achieve a high mechanical strength as well as a suitable biocompatibility of the system (2).

We have previously studied the tape casting process to produce porous zirconia substrates using starch and an acrylic latex emulsion as fugitive additive and binder, respectively (3). Besides, the processing of stable concentrated aqueous FA suspensions with the addition of ammonium polyacrylate (NH₄PA) and Poly(vinyl)alcohol (PVA) as dispersant and binder, respectively, was investigated (4). In this work, porous Y-PSZ tapes with two different volume fraction of porosity (12.7 and 31.4 vol.%) were produced by tape casting and characterized with specific attention directed to the microstructure of the top and bottom surfaces of the sintered tapes. Then, sections of these tapes were dip coated into a concentrated aqueous FA slurry to produce thin FA layers.

Two mechanisms govern the formation of a layer on a porous body during dip coating: liquid entrainment and slip casting. The withdrawal velocity and the suspension properties (volume fraction of solids, viscosity) have influence on the liquid entrainment mechanism; and the microstructure of the substrate (porosity and pore diameter) together with the suspension properties have influence on the slip casting mechanism. In this work, the withdrawal velocity and suspension properties were fixed, therefore the influence of the porous structure of the tape surfaces, top and bottom, on the casting rate and consequently on the layer thickness formed on each surface was studied. Layers formed on the top and bottom surfaces of the tapes with 12.7 and 31.4 vol.% porosity were compared.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Y-PSZ tapes

A commercial 3 mol% yttria- partially stabilized zirconia doped with 0.3 wt% AI_2O_3 (Saint-Gobain ZirPro, Chine) was used to produce the cast tapes. The mean

particle diameter and the specific surface area were 0.15 μ m and 12.25 m²/g, respectively. Potato starch commercially available in Argentina was used as pore former agent. The starch granules exhibit a small degree of anisotropy with a median equivalent diameter of about 50 μ m.

A commercial ammonium polyacrylate (NH₄PA) solution (Duramax D 3500, Rohm & Haas, Philadelphia PA) was used as a dispersant. The binder was an acrylic latex emulsion (Duramax B1000, Rohm & Haas, Philadelphia PA) with solids loading of 55 wt. %, an average particle size of 0.37 μ m, and a glass transition temperature of -26 °C.

FA slurries

The Ca₃(PO₄)₂ (Fluka, Germany) and CaF₂ (Sigma–Aldrich, Ireland) powders were mixed in stoichiometric ratio and calcined 3 hs at 1000 °C. Then, the powder was milled in an attrition mill using 1.6 mm zirconia balls during 48 hours. The milled powder was washed with distilled water and dried at 100 °C. This powder subsequently referred as FA was used to prepare the suspensions for dip coating. NH₄PA and a 9 wt% PVA solution were used as deflocculant and binder, respectively.

2.2 Slip preparation

Y-PSZ tapes

Concentrated aqueous Y-PSZ suspensions with a solid loading of 77 wt.% were prepared by deagglomeration of the powder in distilled water with 0.3 wt.% NH₄PA (dry weight base of powder) using an ultrasonic bath. For the tapes prepared with starch, 13 wt% of starch (dry weight base of Y-PSZ powder) was added to the stabilized Y-PSZ slips followed by ultrasonic treatment. Subsequent to this, 25 wt.% latex (dry weight basis with respect to (Y-PSZ + starch) powders) was added to the slurry, followed by additional stirring. The pH of the suspensions was adjusted to 9.0 with ammonia (25 wt.%).

FA slurries

27.4 vol.% aqueous FA slips with 0.6 wt% NH₄PA and 5 wt% PVA were prepared by suspending particles in deionized water via 20 min of ultrasound; the pH was manually adjusted to be maintained at 9.

2.3 Tape casting, burnout and sintering

The Y-PSZ slips were cast manually on a Mylar film using an extensor. The gap between the extensor and the film was adjusted to 0.4 mm. The cast tapes were subsequently dried in air at room temperature up to constant weight; afterwards, they were stripped from the film and sectioned into rectangular pieces of 2.75 cm x 1.65 cm. The burn out of organic additives was achieved by slow heating (1 °C/min) up to 1000 °C. Then, the pre-calcined tapes were sintered at 1500 °C for 2 h, with a heating rate of 5 °C/min.

2.4 Characterization

Y-PSZ tapes

For the tapes prepared with starch, the volume fraction of starch in the green tape was 16.6%. The bulk sintered density was calculated from the dimensions and weight of the sintered pieces. The microstructure of sintered samples were observed on both the top side of the tape (exposed to air during casting/drying), and the bottom side (exposed to the carrier surface during casting/drying) using a scanning electron microscopy (SEM) (JEOL, JSM-6360).

FA slurries

The viscosity of 27.4 vol.% slips with 0.6 wt% NH₄PA and 5 wt% PVA was measured. Steady state flow curves were performed by measuring the steady shear stress value as a function of shear rate in the range of 0.5 to 542 s⁻¹using a concentric cylinder viscometer (Haake VT550, Germany) at 25 °C.

2.5 Dip coating and characterization of dip-coated tapes

The sintered tapes were vertically dipped into the FA suspension; after immersion during different times they were withdrawn from the suspension. All specimens were immersed and withdrawn at a constant rate of 8 mm/s. The dipcoated samples were allowed to dry at room temperature in the vertical orientation, further dried in air at 60 °C, heated for 30 min at 600 °C for binder burn out and sintered at 1200 °C for 1h. Dipped tapes were diamond polished and examined by SEM; the layer thickness on the top and bottom surfaces were measured.

3. RESULTS AND DISCUSSION

3.1. Characterization of Y-PSZ tapes

The relative sintered density of the tapes prepared with and without starch was 68.6 and 87.3 % of the theoretical density, respectively. The tapes prepared without starch did not achieve full densification at 1500 °C; this observation was also noted for the porous tapes prepared with starch. Figure 1 shows the top surface matrix of a tape with 16.6 vol.% starch sintered at 1500 °C.



Fig.1: SEM micrograph of the top surface matrix for a tape prepared with 16.6 vol.% starch sintered at 1500 °C.

The micrograph show rounded and elongated pores with length between 0.6 and 3.0 μ m. The coalescence of the latex particles during drying and the pore coalescence during sintering might contribute to the enlargement of the pores in the matrix. The large pores in the matrix reduced the sinterability of the Y-PSZ leading to retained closed porosity in the sintered tapes.

The total bulk porosity of the tape prepared with starch (31.4%) was higher than the volume fraction of starch in the green tape (16.6%). Since a full densification of the Y-PSZ matrix did not occur the remaining porosity did not correspond to the volume fraction of starch originally added. Therefore, the higher porosity observed with respect to the amount of added starch was due to an incomplete densification of the Y-PSZ matrix during sintering (Fig.1).

The total bulk porosity of the tapes prepared with starch sintered at 1500 °C followed the V_S + P₀ (F_{VL}/F_{VZ} / F_{VL0}/F_{VZ0}) equation; where P₀ is the total porosity of the tapes without starch, F_{VL} = volume of latex / volume of solids and F_{VZ} = volume of Y-PSZ / volume of solids; thus the factor (F_{VL}/F_{VZ} / F_{VL0}/F_{VZ0}) is the F_{VL}/F_{VZ} ratio of the

green tapes with starch with respect to that of the tapes without starch. The term P₀ ($F_{VL}/F_{VZ} / F_{VL0}/F_{VZ0}$) represents the additional porosity produced by the latex volume added with respect to the Y-PSZ which increased as the starch was added. Clearly, the total porosity of the tapes prepared with starch followed that predicted based on the volume fraction of starch in the green tape plus the additional porosity created by the adjustment of the formulation (high F_{VL}/F_{VZ} ratio for the tape with starch). Figure 2 shows a SEM image of a sintered tape prepared with 16.6 vol.% starch.



Fig.2: SEM micrograph of a sintered tape prepared with 16.6 vol.% starch.

Some of the pores left by the starch interacted and an open structure interconnecting the coarse pores was established. The interconnection open paths and channels between pores which finally result in open porosity (3).

Figure 3 shows micrographs of the top and bottom surfaces of a sintered tape prepared with 16.6 vol.% starch.





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Fig.3: SEM micrographs of the surfaces of a sintered tape developed with 16.6 vol.% starch: (a) top surface; (b) bottom surface; (c) top surface matrix; (d) bottom surface matrix.

The structures of the top and bottom surface matrix are shown in Figs. 3c and 3d, respectively. As we have mentioned the top surface was exposed to air during drying while the bottom one was in contact with the film carrier. The surfaces were different; a greater number of large pores created by the starch particles (lengths between 15 and 80 μ m) (Figs. 3a and 3b) and also a greater number of smaller pores in the matrix (lengths between 0.6 and 3.0 μ m) (Figs. 3c and 3d) were found on the top surface with respect to those on the bottom one. The starch particles migrated to the top surface during casting due to its lower density (1.45 g/cm³) in comparison with 6.05 g/cm³ for Y-PSZ. In addition, during drying the water flow occurred from the top surface of the tape. The consolidation of the latex particles by coalescence is expected to occur in the later stage of the drying process as the volume fraction of latex particles approaches 0.6 (5). This resulted in the formation of latex particle clusters that migrated in the same direction as the solvent, to the top surface, as drying proceeded. Therefore, the top surface matrix of the cast tapes could be comprise by an assembly of latex particle clusters which increased the pore size left during burnout. These large pores reduced the Y-PSZ sintering rate within the matrix leading to retained closed porosity in the sintered tapes. The migration of the starch and the consolidated latex particles to the top surface during casting and drying, respectively, were responsible for the difference in porosity between the top and bottom surfaces of the tape, resulting in an increase in the number of pores.

Figures 4a and 4b show micrographs of the top and bottom surface matrix of a sintered tape without starch.

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Fig.4: SEM micrographs of the surfaces of a sintered tape prepared without starch: (a) top surface matrix; (b) bottom surface matrix.

Minor porosity difference between the two surfaces could be expected since the microstructure only consisted of the small pores in the matrix. The addition of starch to the green tape markedly increased the porosity on the top surface which consisted of pores left by the starch with some connecting channels between them and the pores in the matrix. On the contrary, the porosity on the top surface of the tape without starch was composed only by a lower amount of pores in the matrix (low F_{VL}/F_{VZ} ratio for the tape without starch) (Figs 3a, 3c and 4a).

3.2. Fluorapatite surface coating

Two mechanisms govern the formation of a layer on a porous body during dip coating. The first mechanism is known as liquid entrainment, and ocurrs as the platelike specimen is withdrawn from the slurry faster than the liquid can drain from its surface, leaving a thin slurry film (6). This film thickness, h, is given by:

h=0.94
$$(\gamma/\delta g)^{1/2} Ca^{2/3}$$
 (A)

Ca is the capillary number given by (6):

Ca=
$$\eta$$
 V/ γ (B)

where γ is the surface tension, δ is the slurry density, g is the gravity acceleration, η is the slurry viscosity and V is the withdrawal velocity. As the liquid from the thin layer of slurry evaporates, a thin coating of ceramic particles remains on the surface of the specimen. The second mechanism is a slip-casting phenomenon and occurs because the tapes, when dipped, are slightly porous and dry. The capillary suction

caused by the porous substrate drives ceramic particles to concentrate at the substrate-suspension boundary, and a wet membrane, or cake, is formed, as in the slip casting process (7). In this capillary filtration, the driving force is the capillary suction pressure caused by all the pores on the surface of the substrate. Fluid flow through the consolidated layer and into the porous body is governed by Darcy's law, which can be integrated and simplified (assuming that the permeability of the substrate is much larger than that of the layer) to express the thickness of the sintered layer,L, as a function of time, t, in the form (7):

L=2
$$\beta$$
 ($\epsilon_s \gamma k_m t/\eta \alpha R$)^{1/2} (C)

 β and α are defined as:

$$\beta = \varphi_{m} / (1 - \varepsilon_{m}); \alpha = (\varphi_{0} / \varphi_{m}) - 1$$
(D)

where ϕ_0 and ϕ_m are the volume fraction of the particles in the suspension and in the wet layer, respectively, ϵ_m is the porosity of the sintered layer, ϵ_s is the porosity of the substrate, k_m is the permeability of the wet layer and R represents the pores radius.

The equation (C) shows that when the suspension and substrate are fixed, the layer thickness squared increases linearly with the dipping time. It also implies that the structure of the porous substrate and layer, and the properties of the suspension have close relation to the layer formation process. When the properties of the suspension (solid volume fraction, viscosity) and the structure of the layer remain constant, the porosity and pore diameter of the substrate have much influence on the layer formation.

Figures 5a and 5b show the layer thickness and the layer thickness squared, respectively, versus immersion time for the top and bottom surfaces of the different tapes dip coated in the same fluorapatite suspension (27.4 vol.%, η 106 mPa.s at 542 s⁻¹). The increase in the immersion time produced significantly thicker layers up to reaching saturation of the tapes at 120 s. A linear relation between the thickness squared and the dipping time up to 120 s was found (Fig. 5b), suggesting that these data were in good agreement with the equation (C) for the casting mechanism. The lines in Fig. 5b did not pass through the origin instead they intersected the y- vertical axis at the same thickness value of about 2.5 μ m; as we have previously mentioned the first mechanism in the layer formation was the liquid entrainment which leaved a thin slurry film on the tape surface (eq. A). As the data for the different substrates were obtained by using identical withdrawal velocity and suspension, the same

thickness of the film adhered, h, could be expected. Thus, the film thickness given by eq. (A) was not dependent on the structures of the porous surface. These results indicated that liquid entrainment was the dominant mechanism for layer formation at the initial stage.

A different slope of the lines for the top and bottom surfaces of the tapes prepared with and without starch was found (Fig. 5b). For each tape, the slope was higher for the top surface compared with that for the bottom one. Thus, the casting rate at the top surface of each tape was greater than that at the bottom surface. This behavior could be explain by examining the microstructure of the surfaces (Figs. 3 and 4). For the tapes prepared with starch, a greater number of large pores created by the starch particles and also a greater number of smaller pores in the matrix were found on the top surface with respect to those on the bottom one. The greater porosity and the larger number of smaller pores increased the casting rate (eq. C) of the top surface producing thicker dip-coated layers.



Fig.5: Layer thickness (a) and layer thickness squared (b) versus immersion time for the top and bottom surfaces of the different tapes dip coated in the same fluorapatite suspension.

The absence of starch in the green tape reduced the porosity difference between the two surfaces (Figs. 4a and 4b) since the tape had only a lower amount of the small pores in the matrix, which were principally located on the top surface. As a consequence, minor difference in the casting rate between the two surfaces was observed for the tapes produced without starch (Fig.5). Layers formed on the top surface were found to be about 55 and 32 % thicker than those formed on the bottom surface, for the tapes developed with 16.6 and 0 vol.% starch, respectively.

Figure 6 shows a micrograph of a sintered tape prepared with starch coated with fluorapatite. It showed the thinner dip-coated layer formed on the bottom surface relative to that on the top one. The highest casting rate at the top surface of the tape prepared with starch produced the thickest layer of about 17 μ m.



Fig.6: SEM micrograph of a sintered tape prepared with starch coated with fluorapatite (immersion time = 180 s): (a) bottom surface; (b) top surface.

4. CONCLUSIONS

Thin fluorapatite layers on porous Y-PSZ substrates have been fabricated by dipping porous zirconia tapes into aqueous 27.4 vol.% fluorapatite slurries. Porous Y-PSZ tapes with 31.4 vol.% were developed using starch and an acrylic latex as fugitive additive and binder, respectively. For comparison, Y-PSZ tapes with 12.7 vol.% porosity were fabricated without starch. The casting rate at the top surface of both tapes was greater than that at the bottom surface. This difference was attributed to the greater porosity of the top surface with respect to that of the bottom one and was more pronounced for the tape prepared with starch. For these tapes, the

migration of the starch and the consolidated latex particles to the top surface during tape casting and drying, respectively, resulted in an increase in porosity of the top surface after sintering relative to that of the bottom surface. While for the tapes developed without starch, only a lower amount of consolidate latex particles migrated to the top surface during drying; thus, minor difference in porosity and consequently in the casting rate between the top and bottom surfaces was observed. Layers formed on the top surface were found to be about 55 and 32 % thicker than those formed on the bottom surface, for the tapes prepared with 16.6 and 0 vol.% starch, respectively.

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