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Corrosion behavior and mechanical properties of bioactive sol-gel coatings on titanium implants

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ABSTRACT

Organic–inorganic hybrid coatings based on zirconia and poly (ε-caprolactone) (PCL) were prepared by means of sol-gel dip-coating technique and used to coat titanium grade 4 implants (Ti-4) in order to improve their wear and corrosion resistance. The coating chemical composition has been analysed by ATR-FTIR.
The influence of the PCL amount has been investigated on the microstructure, mechanical properties of the coatings and their ability to inhibit the corrosion of titanium.
SEM analysis has shown that all coatings have a nanostructured nature and that the films with high PCL content are crack-free.
Mechanical properties of the coatings have been studied using scratch and nano-indentation tests. The results have shown that the Young's modulus of the coatings decreases in presence of large amounts of the organic phase, and that PCL content affects also the adhesion of the coatings to the underlying Ti-4 substrate. However, the presence of cracks on the PCL-free coatings affects severely the mechanical response of the samples at high loads.
The electrochemical behavior and corrosion resistance of the coated and uncoated substrate has been investigated by polarization tests. The results have shown that both the coatings with or without PCL don't affect significantly the already excellent passivation properties of titanium.

1. Introduction

Titanium and its alloys are attractive metallic materials widely used as implants for orthopedic dental and orthodontic wires due to their excellent biocompatibility and corrosion resistance even in very aggressive environments. This aspect is related to their ability to form spontaneously a dense and stable titanium dioxide layer on the surface which provides a barrier between the bio-environment and implant [1]. However, the poor tribological behaviour caused by a high and unstable friction coefficient, the poor wear resistance and the strong tendency to seize [2,3] have restricted applications of titanium as a biomedical implant material. Indeed, when local mechanical abrasion removes the protective oxide film, the corrosion resistance of titanium alloys can be strongly decreased [4]. To avoid the early failure of the implants due to wear and corrosion and to extend the prostheses lifetime, different strategies can be followed, such as to increase the thickness of oxide films using nitric acid passivation protocols [4,5] or to apply a protective coating, which also permits to improve the substrate performances related to its surface, as bioactivity and biocompatibilty.

The sol-gel dip-coating process is a promising technique for the deposition of functional coatings at low cost on a wide range of substrates. Sol-gel technology is the process of making ceramic and glass materials at a relatively low temperature which allows the entrapping of various inorganic, organic substances and biomolecules in a glassy matrix during its formation [6].

Ten years ago, Guglielmi [7] has already discussed the potential of sol-gel coatings as a corrosion inhibiting system for metal substrates. Since then, various sol-gel based protective coatings were developed.

In this work, organic–inorganic hybrid materials based on zirconia (ZrO_2) and poly (ε-caprolactone) (PCL) were synthesized by sol-gel method and used, in sol phase, to dip-coat commercially pure titanium grade 4 (Ti-4) implants in order to improve their biological properties and to decrease wear and corrosion.

ZrO_2 has a high expansion coefficient very close to many bulk metals, which can reduce the formation of cracks during the high temperature curing process. ZrO_2 also shows good chemical stability and high hardness which makes it a good protective material [8]. However, inorganic sol-gel coatings have many limitations, as brittleness and high temperature treatment. Many works report the introduction of an organic component into the inorganic sol-gel to form an organic–inorganic hybrid sol-gel coating to overcome these limitations [8,9]. For that purpose, the authors have used the poly (ε-caprolactone) a biodegradable,

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synthetic, aliphatic polyester that has attracted a wide interest for its possible applications as a biomaterial: PCL-based three-dimensional scaffolds for orthopaedic surgery [10], and film substrates for tissue engineering [11] have been proposed. Moreover, composite substrates for tissue engineering have been prepared by sol-gel method, consisting of a poly (ε-caprolactone) matrix reinforced with sol-gel synthesized PCL/TiO_2 or PCL/ZrO_2 hybrid fillers [12,13] as well as several PCL-based hybrids for drug delivery, using different oxides, CaO and/or SiO_2 [14–18], TiO_2 [19,20], and ZrO_2 [21,22]. Moreover, elsewhere the authors proved that such polymer is able to improve the mechanical properties of TiO_2-based glassy matrix [20] and acts as plasticizer in the coatings preparations [9].

The Authors [23] already proved that a ZrO_2/PCL hybrid coating can be used to modify the surface of Ti-4 implants by improving their biological properties (bioactivity and biocompatibility).

The aim of this research is also to investigate the adhesion and the mechanical properties of the synthesized thin films and the corrosion resistance of the Ti-4 implants after coating with the prepared hybrid, when exposed to aggressive human physiological fluids and calcium phosphate surface deposits by means of electrochemical polarization tests, as reported in literature [24]

2. Materials and methods

2.1. Sol-gel synthesis

Hybrid organic–inorganic composites, consisting of an inorganic ZrO_2 matrix and PCL as organic phase were synthesized by means of the sol-gel process. In order to study the influence of the PCL amount on corrosion behavior and mechanical properties of the coatings several films containing different percentage of the polymer was prepared, as shown in Table 1.

Zirconium propoxide $Zr(OC_3H_7)_4$ and poly (ε-caprolactone) (PCL Mw = 65000) were respectively used as inorganic and organic precursors. The solution of poly (ε-caprolactone) in chloroform was added to the solution of $Zr(OC_3H_7)_4$ in ethanol–acetylaceton-water mixture. Acetylacetone was added to control the hydrolytic activity of zirconium alkoxide. After the addition of each reactant, the solution was stirred with a magnetic stirrer and the resulting sols were uniform and homogeneous. The time of gelation was 8–18 days depending on the system. Fig. 1 shows the flow-chart of the hybrid synthesis by the sol gel method. After gelation the gels were air-dried at 50 °C for 24 h to remove the residual solvents. That treatment allows to obtain glassy pieces of various sizes (see Fig. 2) without modifying the stability of the polymer, as its melting temperature is about 65 °C.

2.2. Coating procedure

The hybrid ZrO_2/PCL materials synthesized by sol-gel process, before gelation, when they were still in a sol phase, were used to coat titanium grade 4 (Sweden & Martina, Padua, Italy) disks of 1 cm diameter.

Thin films were obtained by means of the dip-coating technique and a KSV LM dip coater was used. The substrates were ultrasonically cleaned with acetone and were subjected to the passivation process with HNO_3 65%, for 60 min. After passivation, the disks were dip-coated in a ZrO_2/PCL hybrid synthesized solution. The withdrawal speed of the substrate was 15 cm/min. The coated substrates were heat-treated at 45 °C for 1 day to promote a partial densification of the film without any polymer degradation.

The obtained layers appear to be transparent, uniform and crack-free for Zr (1)-(2)-(3)-(4), while cracks appear on the surface of Zr(0). That observation was confirmed by a microstructural analysis performed using SEM (Quanta 200, FEI Europe Company, Netherlands).

Table 1
Label and composition of the prepared coatings.

Label	Composition
Zr(0)	ZrO_2
Zr(1)	ZrO_2 + PCL 5 wt%
Zr(2)	ZrO_2 + PCL 10 wt%
Zr(3)	ZrO_2 + PCL 20 wt%
Zr(4)	ZrO_2 + PCL 30 wt%

2.3. Materials and coating characterization

Scanning electron microscopy (SEM) and Attenuated total reflectance—Fourier transform infrared (ATR-FTIR) spectroscopy were employed to characterize obtained coatings.

The microstructure of the films was investigated by a SEM FEI Quanta 200 equipped with EDX (energy dispersive X-ray spectroscopy).

ATR/FT-IR allows to analyze the chemical composition of the coating surface. The spectra were recorded on a Prestige-21 FTIR spectrometer equipped with an AIM-8800 infrared microscope (Shimazu, Japan), using the incorporated 3-mm diameter Ge ATR semicircular prism. The spectra were recorded using an incident angle of 30° with the sum of 64 scans at a resolution of 4 cm^{-1} and in the 650–4000 cm^{-1}. The spectra were elaborated by Prestige software (IRsolution).

2.4. Mechanical characterization techniques

Scratch tests were carried out on a CSM Micro-Combi tester. In those tests, a controlled scratch on the coating surface was made with a diamond tip (Rockwell C diamond scratch indenter with tip radius of 200 μm). The tip was drawn across the coated surface of the sample under an increasing load (from 0.1 to 20 N) at a load rate of 4.98 N min^{-1} along a scratch length of 1 mm. The instrument was equipped with an integrated optical microscope, an acoustic emission detection system and a device to measure the tangential frictional force in the scratch direction. The sensors allowed to determine the critical load (LC1), evaluated as the normal load at which the first damage occurred to the coating. Three scratches were carried out in different zones for each specimen and the average value of the critical load was evaluated.

Nanoindentation was performed using a Berkovitch indenter (Nanoindenter, CSM Instruments, Peseux, CH) operating at a constant load of 50 mN (loading and unloading rate = 360 mN/min), applied for 15 s, in order to maintain the indentation depth below 1 μm. A second set of nanoindentations was performed in penetration depth control, imposing a maximum penetration depth of the indenter equal to 100 nm. Nanoindentation results were analyzed according to the Oliver and Pharr procedure [25] in such a way as to determine the coating hardness and elastic module. The same penetration depth vs. load curves were also used to evaluate the amount of work required to cause the nanoindentation, and the percentage of work performed in the elastic regime (integral of the unloading curve) or plastic regime (difference between the integral of the loading curve and the unloading curve). Ten nanoindentations were performed in different zones of each specimen, and the average values were evaluated.

Four specimens belonging to the same ZrO_2 + 10 wt% PCL series were used to assess the reproducibility of measurements, and preliminary results indicated that the within sample variations resulted larger than the variations between samples. Hence a mechanical testing was performed on two specimens per series, in different regions of the coating.

2.5. Corrosion tests

The accelerated corrosion tests were performed in an electrochemical cell (Flat Cell K0235 PAR), using the samples as working electrode (exposing a flat and circular area of area of 1.6 cm^2), a platinum grid as counter electrode and an $Ag/AgCl/KCl_{(sat.)}$ electrode (SSCE) as