Materials Science and Engineering C 74 (2017) 501–507

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Modification of Ti6Al4V implant surfaces by biocompatible TiO_2/PCL hybrid layers prepared via sol-gel dip coating: Structural characterization, mechanical and corrosion behavior

Michelina Catauro [a,*], Flavia Bollino [a], Roberto Giovanardi [b], Paolo Veronesi [b]

[a] *Department of Industrial and Information Engineering, Second University of Naples, Via Roma 21, 81031 Aversa, Italy*
[b] *Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, Via Vivarelli 10, 41125 Modena, Italy*

ARTICLE INFO

Article history:
Received 26 July 2016
Received in revised form 18 October 2016
Accepted 11 December 2016
Available online 13 December 2016

Keywords:
Sol-gel process
Organic-inorganic hybrid materials
Dip coating technique
Scratch test
Corrosion behavior

ABSTRACT

Surface modification of metallic implants is a promising strategy to improve tissue tolerance, osseointegration and corrosion resistance of them. In the present work, bioactive and biocompatible organic-inorganic hybrid coatings were prepared using a sol-gel dip coating route. They consist of an inorganic TiO_2 matrix in which different percentages of poly(ε-caprolactone) (PCL), a biodegradable and biocompatible polymer, were incorporated. The coatings were used to modify the surface of Ti6Al4V substrates in order to improve their wear and corrosion resistance. The chemical structure of the coatings was analyzed by attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy. Coating microstructure, mechanical properties and ability to inhibit the corrosion of the substrates were evaluated as a function of the PCL amount.

Scanning electron microscopy (SEM) showed that the polymer allows to obtain crack-free coatings, but when high percentages were added uncoated areas appear. Nano-indentation tests revealed that, as expected, surface hardness and elastic modulus decrease as the percentage of polymeric matrix increases, but scratch testing demonstrated that the coatings are effective in preventing scratching of the underlying metallic substrate, at least for PCL contents up to 20 wt%.

The electrochemical tests (polarization curves acquired in order to evaluate the corrosion resistance) allowed to asses that the coatings have a significant effect in term of corrosion potential (E_{corr}) but they do not significantly affect the passivation process that titanium undergoes in contact with the test solution used (modified Dulbecco's phosphate-buffered saline or DPBS).

1. Introduction

The combination of an excellent tensile and fatigue strength, osseointegrative properties and corrosion resistance make commercially pure titanium and titanium alloys materials of choice for many orthopedic and dental implant applications. The most commonly used is the Grade 5 Titanium, a titanium alloy referred to as Ti-6Al-4V because of its composition (6% Al and 4% V). Aluminium and Vanadium act as stabilizers of the two allotropic phases of titanium (hexagonal α-phase and cubic β-phase), promoting the oxidation resistance and strength of the implant, respectively. However, the use of this material as implant presents some main drawbacks. Its elastic modulus is higher than that of human bones: this can induces stress shielding and the failure of implant due to bone resorption. The low wear resistance can cause the release of debris and Al or V ions which can induce cytotoxicity or adverse tissue reactions. Moreover, as Ti6Al4V is a biologically inert material, it doesn't induce allergic reaction. However, the body recognizes those implants as foreign and isolates them in a fibrotic capsule. Therefore, the osseointegration is hampered and the prostheses mobilization and failure is induced. To improve the lifetime of the titanium implants, their surface can be modified by applying a coating of bioactive and biocompatible glasses or glass-ceramics [1,2]. This strategy allows retaining the favorable mechanical properties of titanium, favor its integration process improving the biological properties, inhibit wear, corrosion and ion release [3–9]. Sol-gel dip coating technique is an ideal technology to coat a wide range of substrates with bioactive and biocompatible glassy materials [2].

Sol–gel is the method used to synthesize ceramic and/or glass materials at a relatively low temperature [10] through the hydrolysis and condensation of metal alkoxide precursors. Sol-gel materials are provided of intrinsic bioactivity [11,12]. The hydrolysis reaction, indeed, generates —OH groups which are able to induce the hydroxyapatite nucleation in vitro and in vivo. The sol-gel method can be easily coupled with a range of coating techniques. When the dip coating method is used, a substrate is dipped into the starting colloidal solution (the

---

* Corresponding author.
E-mail address: michelina.catauro@unina2.it (M. Catauro).

http://dx.doi.org/10.1016/j.msec.2016.12.046

'sol') and withdrawn at a constant speed to enable the sol drainage and its instantaneous gelation. The thickness and the morphology of the coatings is strongly influenced by the withdrawal speed and the viscosity of the sol, which must be carefully chosen [10,13]. Many works reports the use of sol-gel coatings also as protective systems able to inhibit corrosion of metal substrates [6,14].

The main limit of the inorganic sol–gel coatings is the brittleness. To overcome this drawback an organic component can be embedded into the inorganic sol–gel matrix to form an organic–inorganic hybrid sol–gel coating [6]. Organic–inorganic hybrid nanocomposite materials are homogeneous bicomponent systems in which the two components interact at the molecular level. Their properties derive from the synergic effect between the properties of each component. They can be easily obtained using the sol-gel technique by entrapping various organic polymers in a glassy matrix [15,16]. The low processing temperature used during the sol-gel process, indeed, makes this technology compatible with thermolable molecules.

In the present work, organic-inorganic hybrid coatings, consisting of a titania (TiO_2) inorganic matrix and organic poly (ε-caprolactone) (PCL), are prepared by means of the sol-gel dip coating technique and used to modify the surface of Ti6Al4V implants in order to improve their performances. The main idea in the development of such coatings was to combine the known anticorrosive properties of the titania with the mechanical properties of the polymer. It is known, indeed, that the high corrosive resistance of titanium and its alloys is due to the spontaneous formation of a dense and stable titanium dioxide surface layer which constitutes a barrier between the implant and the surrounding tissue [17]. However, local mechanical abrasion can lead its removal and, thus, a strongly decrease of the corrosion resistance [18]. Therefore, to avoid the early failure of the implants due to wear, the thickness of oxide layer can be increased using nitric acid passivation protocols [18,19] or a protective layer can be applied. In the present work, the application of synthetic TiO_2-based sol-gel coatings is proposed for this purpose.

On the other hand, PCL is a biodegradable and biocompatible aliphatic polyester. Elsewhere [20], an improvement of mechanical properties of TiO_2-based sol-gel glasses was obtained by adding PCL to the inorganic matrix. The addition of PCL also allowed to obtain crack-free organic-inorganic coatings [7].

Elsewhere [21] it was proved that TiO_2/PCL coatings have high bioactivity and biocompatibility and that their application to titanium implants improves their biological performance. In the present work, the adhesion, the mechanical properties and corrosion behavior of TiO_2/PCL coatings were investigated as a function of the PCL content, to evaluate the possibility of using them in biomedical field.

2. Materials and methods

2.1. Sample preparation

Inorganic TiO_2 and inorganic/organic TiO_2/PCL hybrid nanocomposites containing 5, 10, 20 and 30 wt% of the organic component, were synthesized using the sol-gel route as reported elsewhere [21]. Therefore, Titanium(IV) butoxide (TBT, Sigma Aldrich) was used as metal alcoxide precursor of the inorganic matrix, 1-butanol 99.8% (BuOH, Sigma Aldrich) as solvent and glacial acetic acid (HAc, Carlo Erba) as chelating agent to control the hydrolytic activity of titanium alkoxide. To synthesize the hybrid systems, poly (ε-caprolactone) (PCL Sigma Aldrich, $M_w = 65.000$) dissolved in chloroform (CH_3Cl) was added to the inorganic sol in different amounts.

The materials in sol phase, before gelation, were used to coat Ti6Al4V (Titanium Consulting & Trading s.r.l. Milan, Italy) disks of 18 mm diameter and 1.5 mm thickness using a KSV LM dip coater. Before starting the coating process, the substrates were polished (with emery papers, until FEPA P#1000, and emery cloths imbued with a diamond suspension, 3 μm grain size), ultrasonically cleaned with acetone and subjected to a passivation process with HNO_3 65%, for 60 min. To dip coat the disks a withdrawal speed of the substrate equal to 10 mm/min was used. The coated substrates were heat-treated at 45 °C for 24 h to promote a partial densification of the film without any polymer degradation.

2.2. Coating characterization

The chemical structure of the obtained coatings was investigated by Attenuated total reflectance - Fourier transform infrared (ATR-FTIR) spectroscopy. The spectra were recorded using a Prestige-21 FTIR spectrometer equipped with an AIM-8800 infrared microscope (Shimadzu, 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} region. The spectra were elaborated by Prestige software (IRsolution).

The microstructure and the morphology of the obtained coatings were investigated by a scanning electron microscopy SEM FEI Quanta 200 equipped with EDX (energy dispersive X-ray spectroscopy).

2.3. Mechanical characterization techniques

Scratch tests (three scratches per sample) were carried out on a CSM Micro-Combi tester equipped with a diamond tip (Rockwell C diamond scratch indenter with tip radius of 200 μm), applying on the coated surface increasing load (from 0.1 to 20 N) at 4.98 N min^{-1} rate, for an overall scratch length of 1 mm. The on board sensors (load cell for tangential force, acoustic emission transducer and optical microscope) allowed to determine the critical load (LC1), evaluated as the normal load at which the first damage occurred to the coating. Nanoindentation was performed using a Berkovitch indenter (Nanoindenter, CSM Instruments, Peseux, CH) operating at a maximum constant load of 25 and 50 mN (loading and unloading rate = 50 mN min^{-1}) applied for 15 s. The different loading conditions have been chosen in order to investigate possible effects related to the depth of indentation and 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 250 nm. As a matter of fact, SEM observations on fracture surfaces (like the one in Fig. 1) confirmed that the deposited coatings have a minimum thickness of 2.7 μm in the investigated zones, reaching a maximum value of 11.3 μm in case of the 30% PCL samples. Nanoindentation results were analyzed according to the Oliver and Pharr procedure [22], allowing to evaluate the hardness

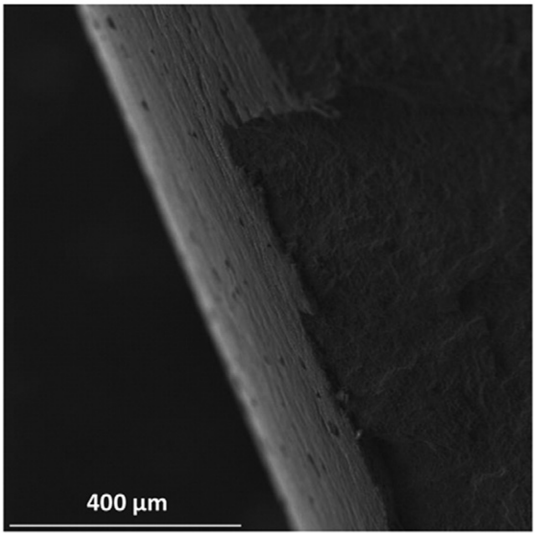

Fig. 1. SEM micrograph of the fracture surface (cross section) of the TiO_2 + PCL 20 wt% coated sample.