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Frictional and adhesive behavior of organic–inorganic hybrid coatings on surgical grade stainless steel using nano-scratching technique

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ABSTRACT

Because of their mechanical properties, metals are the most widely used materials as orthopaedic implants. However they cannot provide a natural bond with the mineralized bone and they also release metallic particles due to degradation or tribologic events. One way to improve the metallic implants performance is to apply protective organic–inorganic sol–gel coatings. In this work, stainless steel substrates are coated with films made by a sol–gel technique from organosilane precursors.

Although mechanical properties of similar films have been studied, there is no information about adhesion, friction or deformation processes of silica-based hybrid films to stainless steel substrates.

Hybrid coatings with higher amount of inorganic components (called TMH) have almost no elastic response and the debris due to chipping or delamination does not persist into the indentation trace. With the film with high content of organic compounds was found elastic recovery in early stages of loading and there is evidence of pile-up at the edges of the trace with higher load applied. After the unloading the film has a persistent deformation and is removed due to the asynchronic recovery of the film and the substrate. The combined two-film coating shows a lot of debris in the trace. This is an unusual but possible behavior of polymeric coatings and could be attributed to different recoveries between the first inorganic layer (called TEOS–MTES), the substrate and the upper TMH film. This fact produces delamination and crack formation in the TEOS–MTES coating, inducing tensile efforts, and finally the upper film is pulled-off.

1. Introduction

A lot of biomaterials are used in medicine, but not all of them can be used for orthopaedic purposes because of the high mechanical properties required. The most widely used materials are inert metals [1]. However, there are problems when is necessary to create a natural union with the mineralized bone and these materials could release metallic particles to the surrounding media. This fact can cause different pathologies that could finally lead to the removal of the implant [2,3]. One way to improve the metallic implant performance consists in the application of protective films [4,5]. These coatings are mainly made from alcoxide precursors of SiO_2 that create vitreous and uniform films. These films can be functionalized introducing particles in the system, or can be bioactive themselves [6–10].

A disadvantage of glassy coatings is their brittleness. The hybrid organic–inorganic films with high content of silica are presented as an alternative to improve the mechanical properties of vitreous coatings preserving an interesting property of them: to be a protective and dense net [11,12]. In addition, the incorporation of hydroxides with some organic groups is expected to give plastic characteristics to the films. In order to make thicker films, coatings with high proportion of organic compounds have been recently obtained. These films are able to contain bioactive particles that are not easily released to the media [13].

These thin films provide the material the capability to be a bio-inert connector between the metallic prosthesis and the bone tissue. Also, superficial features as the roughness or friction coefficient and the adhesion of the coating to the substrate are of great importance for a complete mechanical characterization. Usually, the orthopaedic doctors do not pay special attention in the type of material or if it is a coated one at the time the implant is been inserted in the body. The implanting procedure is performed by applying high tension and loads on the metal. Because of this, it is important to know the mechanical, adhesive and wear properties and behavior of the implant surface in order to avoid future failure of

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the prosthesis. There is no information about the friction coefficient or the adhesion of silica-based hybrid organic inorganic coatings on stainless steel although their Young's modulus and hardness were recently analyzed [14] and mechanical properties of similar films have been studied [15–17].

One of the most recent techniques used to study the mechanical properties of thin films is the instrumented indentation, known as nanoindentation. This is a superficial technique to measure quasi-statically the penetration of an indenter at increasing loads applied to a material. With a modulus of lateral force, and a ramped load in a displacement (scratch) path, the nano-scratching test is implemented [18–22].

The aim of this work is to advance in the knowledge of the frictional and adhesive behavior of organic–inorganic hybrid silica-based thin coatings deposited on stainless steel used in orthopaedic surgery, employing the nano-scratching technique.

2. Experimental procedure

Flat samples of stainless steel AISI 316L were used as substrates. Before the application of coatings, they were successively cleaned in a soap solution and isopropylic alcohol in an ultrasound bath for 5 min. Finally, they were rinsed with distilled water and dried with hot air.

Two types of sols were used to make different coatings: TEOS–MTES and TMH (composed by TEOS–γMPS–HEMA). The starting materials were TEOS = tetraethoxysilane (ABCR); MTES = methyltriethoxysilane (ABCR); γMPS = 3-methacrylopropyl trimethoxysilane (Dow Corning) and HEMA = 2-hydroxyethyl methacrylate (Aldrich).

The TEOS–MTES sol was prepared by acid catalysis method in one stage, using TEOS and MTES as silica precursors; absolute ethanol as solvent and 0.1 N nitric and acetic acids as catalysts. Water was incorporated from the nitric acid solution in stoichiometric ratio. The molar ratio of TEOS/MTES was 40:60. All the reagents were stirred at 40 °C for 3 h obtaining a transparent sol (pH 1–2, viscosity = 2.6 mPa s). The TMH sol was made in a two-step procedure using 0.1 N nitric acid and isopropylic alcohol. The solution, containing 40 g l^{-1} of SiO_2, was stirred at 65 °C for 36 h in a glycerine bath.

Coatings were obtained by dip-coating at room temperature and withdrawn at 25 cm min^{-1}. Three different types of coatings were applied on the stainless steel substrates:

(a) Single coating consisting for one layer of TEOS–MTES sol treated at 450 °C for 30 min in air.
(b) Single coating (double-layer) consisting for two layers of TMH sol applied successively. The first layer was air dried for 30 min at room temperature, and the second layer was air treated for 60 min at 150 °C.
(c) Double coating consisting for a first layer of the TEOS–MTES hybrid, air treated at 450 °C for 30 min (type a), followed by a second double-layer of TMH (type b) coating, air treated for 60 min at 150 °C.

Immediately after film deposition on a glass substrate, a scratch was made with the aim of measuring coating thickness by using a profilometer (Talystep, Taylor-Hobson, UK). The final value was calculated as the average of three measurements.

The nano-scratch tests were performed using a nano-indenter XP, MTS NanoInstruments [23] (force resolution: 50 nN; displacement resolution: 0.1 nm) equipped with a nano-scratch attachment that allows lateral force measurements. A pyramidal diamond Berkovich indenter (tip radius = 1 μm) was used to produce the wear of each coating/substrate system and a 1400 μm scratching track was applied in all tests. The experimental procedure is shown in Fig. 1. At first (pre-scan step), the tip approaches the surface under default conditions, and then the load is maintained (0.1 mN) through all the scratch distances (200 μm initial + 1000 μm straightforward scratch + 200 μm final). An initial surface profile of the samples is made before scratching. In the second step (scratching), the tip starts to scratch at 200 μm from the start of the experiment with a ramped load to the distance of 1200 μm (final maximum applied load of 300 mN), where the load is removed to the initial one (0.1 mN) and maintained constant for 200 μm more. The surface profile could be sensed by the depth-sensing system. In the third step (post-scan) the test is done as was described in the pre-scan to measure the elastic recovery after scratching.

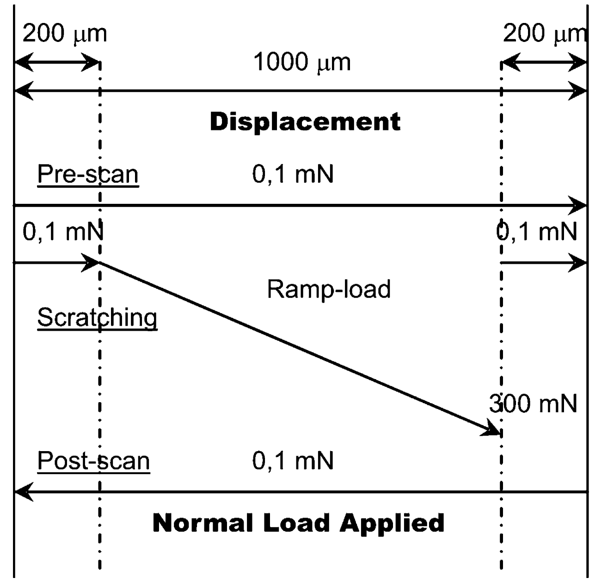

Fig. 1. Schematic diagram of the different steps for the experimental scratch test procedure.

Lateral (friction) forces are calculated from the stiffness measured in the calibration tests using fused silica as model material. The coefficient of friction is calculated by taking the ratio of the lateral force and the normal load applied on the indenter [22].

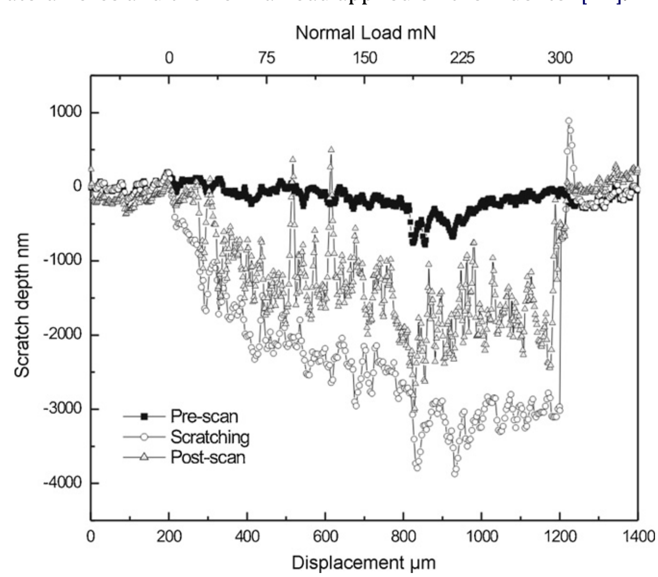

Fig. 2. Scratch depth profile versus normal applied load and horizontal displacement of the indenter tip on the TEOS–MTES coating on surgical grade stainless steel. The pre-scan, scan and post-scan made are shown.