Thin Solid Films 593 (2015) 71–80

Contents lists available at ScienceDirect

Thin Solid Films

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

Study of the mechanical behavior and corrosion resistance of hydroxyapatite sol–gel thin coatings on 316 L stainless steel pre-coated with titania film

Djahida Sidane [a,*], Didier Chicot [b], Sabeha Yala [a], Salima Ziani [a], Hafit Khireddine [a], Alain Iost [c], Xavier Decoopman [b]

[a] Laboratoire de Génie de l'Environnement, Département de Génie des Procédés, Université de Bejaia, Route Targa Ouzemour, Bejaia 06000, Algeria
[b] Laboratoire de Mécanique de Lille, LML, UMR 8107, UST Lille, IUT A GMP, BP 90179, 59 653 Villeneuve d'Ascq, France
[c] MSMP, Arts et Métiers ParisTech, 8, Boulevard Louis XIV, 59000 Lille Cedex, France

ARTICLE INFO

Article history:
Received 17 November 2014
Received in revised form 13 September 2015
Accepted 17 September 2015
Available online 25 September 2015

Keywords:
Hydroxyapatite
Titania
Sub-layer
Mechanical behavior
Corrosion test

ABSTRACT

In order to reinforce the clinical applications of hydroxyapatite (HAP) sol–gel coatings deposited onto 316 L stainless steel, we suggest the introduction of an intermediate thin layer of titania (TiO_2) on the substrate. The titania sub-layer is introduced in order to improve both the corrosion resistance and the mechanical properties of the HAP/316 L stainless steel coated system. The two coatings, HAP and TiO_2, were studied separately and afterwards, compared with the bi-layered coating. A film without any cracks is obtained under the optimum conditions in terms of annealing temperature, dipping rate and aging effect. Microstructural, morphological and profilometry analysis revealed the non-stoichiometric carbonated porous nature of the hydroxyapatite coatings, which were obtained after annealing at 500 °C during 60 min in the atmosphere. The obtained TiO_2 coatings exhibit a dense and uniform surface. Addition of TiO_2 as sub-layer of the HAP coating tends to increase the homogeneity and the crystallinity rate as compared to the HAP one.

The mechanical properties, i.e. hardness and elastic modulus, are determined by means of nanoindentation experiments and the adhesion between the coating and substrate is estimated by scratch tests. The corrosion behavior is evaluated by potentiodynamic cyclic voltammetry tests. As a main result, the values of the elastic modulus and hardness, respectively of 30 GPa and 2.5 GPa, are relatively high for the HAP–TiO_2 bilayer coating. This result allows the use of such coated material as a replacement material for hard tissues. The adhesion strength increased from 2925 mN up to 6430 mN after the addition of the TiO_2 intermediate film. According to the Tafel's analysis, the 316 L stainless steel specimens coated with both HAP and titania layers ($E_{Corr} = -234$ mV, $I_{Corr} = 0.089$ μA cm^{-2}) present a better resistance than the HAP-coated specimens ($E_{Corr} = -460$ mV, $I_{Corr} = 0.860$ μA cm^{-2}).

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Thin titania coatings on 316 L stainless steel have the combined advantages of biocompatibility and corrosion resistance [1,2]. Consequently, the use of Titania as a bonding oxide film between the hydroxyapatite and the substrate is studied with the objective of improving the global properties of the HAP coatings [3–7]. In this work, we propose a strategy of HAP coating with the introduction of TiO_2 oxide ceramic at the surface of the 316 L stainless steel substrate in order to improve the corrosion resistance, the mechanical properties and the bonding strength of the bilayer HAP–TiO_2 bioceramic coating. The coatings were obtained by the sol–gel dip coating process due to its simplicity, and also because it allows the preparation of high-quality thin films on metal substrates [8,9]. Moreover, it has been reported in the literature that the coated materials prepared by sol–gel deposition are more bioactive than those prepared by other methods [10,11]. The main objective of this study is to evaluate the mechanical behavior of sol–gel hydroxyapatite and hydroxyapatite–titania bilayer coatings on 316 L stainless steel.

In a previous work [12], we determined the hardness of the HAP single and the bi-layered coating systems by means of classical microindentation tests. The model of Jönsson and Hogmark was applied to separate the two contributions of the substrate and of the film in the measured hardness in order to determine the hardness of the film only.

* Corresponding author at: Université Abderrahmane Mira, Route Targa Ouzemour, Bejaia 06000, Algeria.
E-mail address: dj.sidane@yahoo.fr (D. Sidane).

http://dx.doi.org/10.1016/j.tsf.2015.09.037
0040-6090/© 2015 Elsevier B.V. All rights reserved.

In this paper, additional studies have been performed using the continuous stiffness measurement mode in nanoindentation in order to determine the hardness of the film as a function of the indenter displacement. Consequently, nanoindentation provides a useful comparison with the mechanical properties of the surrounding coatings and underlying substrate. Various methods can be employed to address the problem of determining the hardness and elastic modulus of thin films when the substrate is involved in the deformation process occurring during the indentation experiments. Only few publications present in detail the determination of the elastic modulus and the hardness of thin hydroxyapatite sol–gel films (<2000 nm in thickness) directly and properly from the indentation data. The determination of the mechanical properties of relatively thin coatings by nanoindentation often requires the application of models for separating the contribution of the substrate from the indentation data [13,14]. For hardness measurements, a model must be applied when the indenter displacement is higher than a given value, which depends both on coating thickness and the mechanical behavior of the coating, i.e. for a hard coating on a soft substrate or for a soft coating on a hard substrate. For example, Bückle [15] and Sun. et al. [16] indicate a value for the indenter displacement close to 10% of the coating thickness after which the substrate interferes with the measurement. Unfortunately, this limit of 10% is not a predictable value. When considering the elastic modulus determination, this limit value can be much less. Indeed, this value is close to 1% of the film thickness for a hard film deposited onto a soft substrate [17,18] and it can reach 20% for a soft film deposited onto a hard substrate [19,20]. As a consequence, to avoid the application of models for which the above mentioned limit values cannot be defined precisely and also for which the accurateness significantly depends on the adjustment of the intrinsic fitting parameters to the model, a direct determination of the mechanical properties of the material will be preferable. This is rendered possible by means of the continuous stiffness measurement mode, which allows the computation of both the hardness and the elastic modulus as a function of the indenter displacement [21]. Moreover, under these conditions, the mechanical properties can be obtained for very low indenter displacements, typically less than 50–100 nm. According to the nature of these variations, application of models may or may not be required. In this work, we suggest the study of the mechanical properties by analyzing the variation of the hardness and the elastic modulus as a function of the indenter displacement.

Regarding the application of coated systems, the adhesion strength between the coating and its substrate is a very important parameter, which must be studied by means of scratch tests. These tests performed with a spherical diamond indenter, allow the determination of the critical load corresponding to the removal of the coating. This critical load can be used as an adhesion criterion.

There is always concern about the corrosion resistance of the 316 L stainless steel in physiological fluids. For this reason, the development of the biomedical implants requires the improvement of their corrosion resistance. In this paper, the influence of the bilayer hydroxyapatite–titania film on the corrosion resistance of the 316 L stainless steel in simulated human body fluids has been examined. The experiments were conducted using open circuit potential and potentiodynamic cyclic voltammetry tests.

2. Materials and experiments

Specific amounts of phosphorus pentoxide (P_2O_5, Prolabo 100%) and calcium nitrate tetrahydrate ($Ca(NO_3)_2.4H_2O$, Fluka 98%) were dissolved in absolute ethanol to form different solutions with concentrations of 0.5 mol/l and 1.67 mol/l, respectively. These two solutions were mixed to obtain the HAP sol having Ca/P molar ratio of 1.67 [22]. The mixture was continuously stirred at room temperature for 24 h. This produces a translucent sol. Titanium isopropoxide (TIP, Fluka 100%) was used as a titania precursor in the sol–gel process. The reactivity toward water is modified by acetic acid (HOAc) (molar ratio of TIP/HOAc = 1/10), which is also used as catalyst. 2-methoxy ethanol was added to adjust the degree of viscosity of the solution. This solution with titanium molar concentration of approximately 0.47 M was vigorously stirred at room temperature [23].

Finally, the resultant HAP sol was closely capped and aged for 24 h at room temperature. In the same way, TiO_2 sol was kept closely capped and aged for 24 h at the temperature of 100 °C. The effect of temperature of TiO_2 aging sol on the film morphology has been discussed and detailed in [12].

316 L stainless steel is used as the substrate. The dimensions of the samples are 20 × 10 × 5 mm. Before deposition, the samples were mechanically polished using different silicon carbide grit papers from 120 to 1200 grades. Mirror polishing was done using diamond paste of 2 μm and of 0.7 μm in the final step. The substrate samples were ultrasonically degreased with acetone and washed with running double distilled water. Finally, they were dried at 150 °C during 10 min. The TiO_2 coatings were obtained by dipping the polished, washed and dried substrates in the suspension at the dipping rate of 20 mm/min and annealed at 450 °C during 60 min. Dipping of the hydroxyapatite suspension was maintained in the range of 10–80 mm/min and annealed at different temperatures, i.e. 500 °C, 600 °C, 700 °C and 750 °C during 60 min in air. The HAP particles were deposited onto the surface of the TiO_2 film with the optimized parameters.

The different phases present in the coatings were identified by X-Ray diffraction (XRD) analysis, (panalytical type MPD/system vertical θ/θ), using radiation source (CuKα = .5406 Å) operating at 40 kV and 30 mA. The XRD diffraction patterns were collected over a 2θ range located between 20° and 80° using an incremental step size of 0.02° with 6 s of acquisition time per step. The identification of the phases was performed by comparing the experimental XRD patterns to standards compiled by the International Center for Diffraction Data (ICDD).

The microstructure analysis for identifying the different species and the functional groups present in the HAP coatings was carried out using a Fourier Transform Infrared (FT-IR) spectrophotometer instrument (IRAffinity-1, SHIMADZU). FT-IR spectra were recorded in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. The deposited films were scraped off as powders from the substrate and mixed with KBr powder (80% in weight) to form an infrared transparent pellet.

The microstructural changes and the elements present at the surface of the coated specimen were studied by means of a scanning electron microscope equipped with energy dispersive X-ray spectroscope (SEM/EDS FTI QUANTA 200, detector SUTW-Sapphire, resolution: 135.25) using the standard EDAX ZAF quantification method on the SEC factor. The SEM was used to examine the morphological features of the coatings. Samples were mounted on individual substrate holders using a carbon adhesive tape.

Both coating thickness and coating roughness were measured using a profilometry analysis "DEKTAK 150 SURFACE PROFILERT". The surface of the coating is scanned at an interval of 1000–8000 μm. Three different areas were scanned and measured to determine a mean value for the thickness and the roughness parameter.

Nanoindentation experiments were performed with a Nano Indenter XP ™ (MTS Nano Instruments) employing a Berkovich diamond indenter. The samples were fixed on a metallic support using the heat softening glue crystalbond 509. 25 indentation tests were conducted randomly on the surface of the material with the same indentation testing conditions. The maximum indentation depth reached by the indenter was fixed at 2000 nm and the strain rate was equal to 0.05 s^{-1}. The instrument was operated in the continuous stiffness measurement (CSM) mode allowing the computation of the elastic modulus and the hardness continuously during the indentation loading. The harmonic displacement was 2 nm and the frequency was 45 Hz. The elastic modulus of the coating, E_C, is deduced from the reduced modulus, E_{RC}, given by the instrument, which takes into account the elastic properties, E_i

Download English Version:

https://daneshyari.com/en/article/1664337

Download Persian Version:

https://daneshyari.com/article/1664337

Daneshyari.com