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The hardness of the hydroxyapatite-titania bilayer coatings by microindentation and nanoindentation testing

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Abstract. The aim of this paper is to investigate the effect of the addition of titania (TiO2) inner-layer on the morphological and mechanical properties of hydroxyapatite (HAP) bioceramic coatings deposited on 316L stainless steel (316L SS) by sol-gel method in order to improve the properties of hydroxyapatite and expand its clinical application. The addition of TiO2 as sub-layer of a hydroxyapatite coating results in changes in surface morphology as well as an increase of the microhardness. The deposition of the inner-layer provides the formation of new types of hydroxyapatite coatings at the same condition of annealing. This represents an advantage for the various applications of the hydroxyapatite bioceramic in the medical field. Classical hardness measurements conducted on the coated systems under the same indentation load (10g) indicated that the microhardness of the HAP coating is improved by the addition of TiO2 inner-layer on the 316L stainless steel substrate. The hardness values obtained from both classical tests in microindentation and the continuous stiffness measurement mode in nanoindentation are slightly different. This is because nanoindentation is more sensitive to the surface roughness and the influence of defects that could be present into the material. Moreover, nanoindentation is the most useful method to separate the contribution of each layer in the bilayer coatings. In this study, the hardness is comparable with those reported previously for pure HAP ceramics (1.0–5.5 GPa) which are close to the properties of natural teeth.

1. Introduction
Hydroxyapatite (Ca10(PO4)6(OH)2, HAP) is widely used for hard tissues repair due to its chemical and structural similarities with the mineral phase of bone and teeth. In this paper, we proposed a strategy of coating 316L stainless steel (316L SS) substrate with HAP ceramic. The sol–gel dip coating process is easily applicable to surface coating, and it allows the preparation of high quality HAP thin films on metal substrates [1, 2]. Many recent studies have investigated the variation of the microstructural and morphological properties of the hydroxyapatite coatings with the influence of the reinforcing process such as the addition of titania (TiO2) phase in order to improve the bioactivity, mechanical, and bonding strength of the nanocomposite coatings developed [3–6]. It is recognized that thin films of TiO2 on 316L SS possess combined advantages of biocompatibility and corrosion-resistant properties [7]. As a simple and direct measurement, indentation hardness is often used as an initial guideline for the qualification of a coating for any application requiring wear resistance. As a rule of thumb, intrinsic film hardness can be directly measured when the penetration depth of the indenter is lower than 10% of the coating thickness. In this case, the substrate is supposed to not interfere in the hardness measurement. For the recent generation of coatings that are becoming thinner and thinner, very often below than 4-5 µm, this rule of thumb is sometimes difficult to be respected mainly in microindentation [8, 9].
2. Experimental details

Defined amounts of phosphorus pentoxide (P₂O₅, Prolabo 100 %) and calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O, Fluka 98 %) were dissolved in absolute ethanol, to form solutions with concentrations of 0.5 and 1.67 mol/l, respectively. The two solutions were mixed and this results in the formation of HAP sol having Ca/P molar ratio of 1.67 [10]. The mixture was continuously stirred at ambient temperature for 24 hours. This produces 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 under ambient temperature conditions [11]. 316L SS substrates were mechanically polished using different silicon carbide grit papers up to #1200 grades. Final polishing was done using diamond paste (2 µm) and (0.7 µm) to produce scratch-free mirror finish surface. The substrates were ultrasonically degreased with acetone and washed with running double distilled water. Finally, they were dried at 150 °C for 10 minutes. The TiO₂ coatings were obtained by dipping the polished, washed, and dried metal substrates in the suspension with dipping rate of 20 mm/min and annealed at the temperature of 450 °C for 60 minutes. The HAP-TiO₂ bilayer coatings were obtained by the deposition of the hydroxyapatite on the outer surface of the TiO₂ single coatings, with dipping rate of 80 mm/min and annealed at the temperature of 500 °C for 60 minutes.

The morphology and the elemental analysis of the surface of the coated specimen were performed using scanning electron microscopy (SEM QUANTA 200, detector SUTW-Sapphire). The thickness of the coating layer was measured using a profilometry analysis “DEKTAK 150 SURFACE PROFILER,” by scanning the surface of the coating at an interval of 1000-8000 µm. Three different areas were scanned and measured to determine the mean thickness.

Vickers microhardness indentations were performed using a Zwick microhardness machine (ZHV10) with a dwell time of 15 seconds applied at the maximum indentation load. Hardness of the coatings is determined under the lowest indentation load available on the instrument, i.e., 10 g, to minimize the influence of the substrate on the hardness measurement. The hardness value was the result of 10 indents measurements to be representative.

Nanoindentation experiments were performed with a Nano Indenter XP ™ (MTS Nano Instruments) with 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 hardness continuously during the indentation loading. The harmonic displacement was 2 nm and the frequency was 45 Hz.

3. Results and discussion

3.1. Morphological properties

Figure 1 shows the SEM images related to the HAP single coating (Figure 1a) and bilayer coating (Figure 1b).

The HAP single coating exhibited a porous surface composed of spherical agglomerates, whereas the surface of the HAP-TiO₂ bilayer appears dense and uniform. SEM surface examination reveals no detectable cracks for these coatings.
3.2. Vickers microhardness

To analyze the homogeneity and the indentation size effect (hardness-load dependence) of the substrate, a series of indentation loads ranging between 10 and 200 g were performed. Table I gives the hardness number computation for each indentation load. As it can be seen, the microhardness of the substrate varies according to the applied load between 133 HV and 168 HV, the hardness values are close enough to consider a mean value, i.e., 150 HV for the substrate hardness.

Table I. Experimental data of the 316L SS substrate as a function of the applied load.

| Load (g) | 10 | 20 | 50 | 150 | 200 |
|----------|----|----|----|-----|-----|
| Hardness (HV) | 155 | 168 | 150 | 149 | 133 |

For characterizing the hardness of the coatings, only indentation experiments using the indentation load of 10 g have been performed. The comparison between the HAP and HAP-TiO$_2$ coatings is acceptable since their coating thicknesses are quite similar, around 2 µm. The hardness value indicated in Table II is a composite hardness taking into account a part of the elasto-plastic response of the substrate [12]. In order to estimate the apparent hardness of the coating, the model of Jönsson and Hogmark [13] is the only model applicable because the calculation has been performed under only one indentation load. This model, which is predictive and not descriptive since all the involved parameters are known, expresses the composite hardness, $H_C$, as a function of the hardness of the substrate, $H_S$, and that of the film, $H_F$, as follows:

$$H_C = H_S + a \cdot (H_F - H_S)$$  \[1\]

Where $a$ is the parameter representing the influence of the film in the hardness measurement, this parameter can be expressed as a function of the indent diagonal, $d$, and the coating thickness, $t$, as follows:

$$a = \frac{2Ct}{d} - \left(\frac{Ct}{d}\right)^2$$  \[2\]

Where $C$ is a constant equals to 0.5 for brittle materials which is the case here since cracks have been observed around the indents in the coatings (data not showed).

Considering $t = 2 \mu m$, the average diagonal value of 9 $\mu m$ for $d$ and the constant $C$ equals to 0.5, the computation of the parameter $a$ leads to 0.21. Applied to Eq. [1] using the hardness value of the substrate of 150 HV and the hardness value of the composite of 235 HV for the bilayer HAP-TiO$_2$ coating and
215 HV for the HAP coating, the approximate Vickers hardness number of the separate coating is found to be close to 555 HV for the bilayer HAP-TiO$_2$ coating, and 459 HV for the HAP coating. This result is interesting but must be verified by nanoindentation employing the continuous stiffness measurement method. Indeed, this methodology will be necessary to separate the contribution of each layer in the composite coatings [14–16].

Table II. Indent diagonals and Vickers hardness number obtained on the different coatings by applying the same indentation load of 10 g.

| Coating      | HAP           | HAP-TiO$_2$   |
|--------------|---------------|---------------|
| Diagonal (µm)| 9.3 ± 0.2     | 8.9 ± 0.3     |
| Hardness (HV)| 215 ± 10      | 235 ± 16      |

3.3. Nanoindentation hardness

Figure 2 represents the hardness variation for the different situations. As it is clearly shown on this figure, the uncoated substrate presents the highest hardness value with a hardness variation, which decreases from 7 GPa, close to the external surface, to 3 GPa toward the core of the material for the highest indenter displacements. The hardness gap is due to the presence of the iron oxide on the surface of the substrate [17].

For the TiO$_2$ coating, we note that the hardness is very similar to that of the substrate except for indenter displacements very close to the outer surface, typically over the first 150 nm in depth. In this region, we applied the model of Jönsson and Hogmark (Eq. [1]) for determining the hardness of the film only. Here $d$ is the indent diagonal:

$$d = 2tg74h$$

Where h is the indentation depth.

Applied to the hardness variation of the TiO$_2$ films and using the hardness values of the substrate, we obtained a value of 3.5 GPa for the hardness of the titania oxide. For information, Fu et al. [18] indicated that the hardness of titania films measured by nanoindentation, can vary to a great extent, between 2 and 18 GPa depending on crystalline nature and microstructure of the films [19,20].

For the HAP coating, we can note that the hardness value is constant for the lowest indenter displacements over 200 nm in depth. In this region, the hardness is close to 1 GPa. After 200 nm in depth, the hardness value increases toward a value of 3 GPa which corresponds to the hardness of the steel substrate. In this zone, the substrate interferes with the hardness measurement. For this coating, no application of model is required since the film hardness has been determined for the lowest displacements of the indenter. Indeed, the hardness has a constant value of 1 GPa for indenter displacements between 100 and 200 nm.

For the HAP–TiO$_2$ coating, it is interesting to note that the hardness value varies between two limits corresponding to the HAP hardness and the substrate hardness, respectively for the lowest and highest indenter displacements. Between these two limits, the benefit of the sub-layer of TiO$_2$ in terms of mechanical properties is clearly visible since the hardness variation is observed between 2.5 GPa at the extreme surface, as compared to only 1 GPa for the HAP coating, until 6 GPa corresponding to the TiO$_2$ coating or steel substrate hardness at only 300 nm. As a conclusion, we showed that the TiO$_2$ sub-layer significantly improves the hardness of the HAP coating. In this study, the hardness is comparable with those reported previously for pure HAP ceramics (1.0–5.5 GPa), which are close to those properties of natural teeth [21].

Above, it is shown that the microhardness of the HAP coating, which is of 459 HV (4.50 GPa) increases with the addition of the TiO$_2$ inner layers, to reach approximately 530 HV (5.19 GPa) for the global HAP-TiO$_2$ bilayer coatings.
Figure 2. Hardness versus the indenter displacement obtained by using the CSM mode of nanoindentation performed on the uncoated substrate, the HAP, TiO$_2$, and HAP–TiO$_2$ coatings.

4. Conclusion
In addition, the hardness values obtained from both classic tests in microindentation and the continuous stiffness measurement mode in nanoindentation are slightly different. This is due to the fact that nanoindentation is more sensitive to the surface roughness and the influence of defects, which could be present in the material. Moreover, nanoindentation is the most useful method to separate the contribution of each layer in the bilayer coatings.

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