STRUCTURAL CHARACTERIZATION OF TiN/HAp AND ZrO_2/HAp THIN FILMS DEPOSITED ONTO Ti-6Al-4V ALLOY BY MAGNETRON SPUTTERING

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Magnetron sputtering în radio frecvenţa (RF) este o tehnică de depunere promiţătoare, prin care se pot produce filme dense şi cu o aderenţă bună. Această tehnică a fost aplicată pentru a depune filme de TiN/HAp şi ZrO_2/HAp pe implanturi de titan. Stratul intermediar de TiN joacă un rol important în îmbunătăţirea adeziunii hidroxiapatitei la substrat şi previne contactul direct al ţesutului cu substratul metalic, în cazul fisurării stratului de hidroxiapatită.

Compoziţia chimică şi structurală a acoperirilor, aderenţa, precum şi grosimea de strat au fost investigate prin analize de difracţie, FTIR şi EDX.

Radio frequency (RF) magnetron sputtering is a promising deposition technique that can produce dense and well-adhered films. This technique was applied to deposit thin TiN/HAp and ZrO_2/HAp films on titanium implants. The TiN interlayer plays an important role in improving adhesion of HAp to substrate and preserve the direct contact of the tissue with metallic substrate in case of possible crack of HAp coating.

The chemical and structural compositions of the coating, adhesion and thickness have been investigated by using XRD, FTIR and EDX measurements.

Keywords: magnetron sputtering, thin films, zirconia, hydroxyapatite, TiN, biocompatibility

1. Introduction

Due of their excellent bio-compatibility and mechanical properties, titanium (Ti) alloys and Ti6Al4V in particular are often used as materials for femoral stems in cementless total hip prostheses [1-4]. Among the advantages of Ti6Al4V alloy, comparatively with other similar alloys used for such applications, we can mention: its superior corrosion resistance, high fatigue strength and low elastic modulus which reduces stress shielding [3-6]. Concerning abrasive and adhesive wear, however, titanium and Ti6Al4V appear to be inferior to other surgical alloys. Various surface modifications have been used for improving the wear and corrosion behaviour of Ti alloys. A variety of ceramic coatings has been

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tested in vitro and also in vivo and used for improving the properties of the metal surface and enhancing bone ingrowths.

Lately, there was an increasing interest in using titanium nitride (TiN) coating to improve the wear properties of Ti6Al4V. It has a high hardness and low friction coefficient, and has been shown to be efficient in reducing the wear.

Hydroxyapatite (HAp) coating was proved to have bioactive properties and hence improving the bonding strength on bone tissue without inducing the growth of fibber tissue. However, the weak adhesion between HAp and metal implants is still the major problem [7].

To take profit of HAp bioactive properties in spite of its problems of brittleness as a bulk material, it can be applied as a multilayer structure such as a HAp/TiN and HAp/ZrO_2 on the surface of metallic implants [8].

The aim of this work was to produce new HAp coatings with titanium nitride and zirconia interlayer beneath, which could improve adhesion and biocompatibility as well as dimension tolerance and mechanical properties due to small thickness of high quality coatings.

Application of the proposed TiN or ZrO_2 interlayer improved the mechanical properties of resistance to cracking and in this way control the biocompatibility of the deposited coatings.

2. Materials and methods

In the present work a comparative study, concerning the properties of TiN/HAp and ZrO_2 thin films deposited onto Ti-6Al-4V, by magnetron sputtering process, has been carried out.

As a substrate material, disks 20 mm in diameter and 5 mm thick were used.

The magnetron system was energized by a RF power source operating at a frequency of 1.78MHz. A discharge power of 250W of magnetron discharge was maintained constant for all experiments.

Three different targets of 110mm in diameter and 3 mm thickness have been used. The targets were as follows:

- 1 titanium target;
- 1 Hydroxyapatite target obtained by pressed powder;
- 1 CaO and MgO stabilized zirconia target.

The HAp and ZrO_2 targets were prepared by cold pressing of corresponding powders in a Cu crucible.

The substrates were ultrasonically cleaned for 10 min. in acetone baths followed by a 10 min cleaning stage in ethyl alcohol. The substrate cleaning implied also a sputtering stage performed prior the deposition. The sputtering was performed in Ar plasma produced by a plasmatron equipped with a tungsten filament. The bias voltage was 0.4 kV and discharge power 250W.

In order to remove the surface contaminants, the targets were also cleaned by sputtering for a period of 30 min. A distance of 30 mm between the target and the substrate was kept constant for all experiments. Previous experiments showed that this distance assures a good uniformity of the coatings thickness.

The coatings were deposited at different ratio between discharge gas pressures and reactive gas (Table 1).

Table 1

Deposition parameters

Sample	Working gas	Pressure (Pa)	Time (min)
HAp	100%Ar	0,3	60
ZrO_2	100%Ar	0,3	60
TiN	50%Ar+50%N_2	0,2	60

After deposition the coatings were heat treated at 550^0C for 1 hour, to induce a phase transition from an amorphous structure to a crystalline structure. The morphology of the coatings, physical and chemical properties and some mechanical characteristics were analyzed.

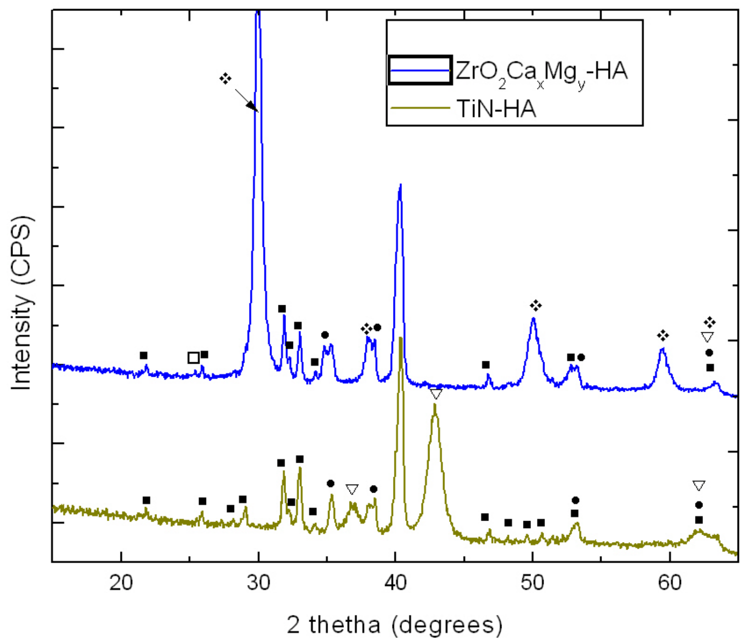
XRD analysis, performed at grazing angle, was used to determine the crystallinity degree of the coatings and to identify the phase composition (Bruker diffractometer with a Cu K_α radiation λ=0.154 nm, investigated range 5-65°, 40KV, 30mA, step 0,04°).

Fourier Transform Infrared Spectroscopy (FTIR) has been used in order to determine the molecular vibrational modes belonging to the main functional groups or to determine the nature of chemical bondings. A Perkin Elmer BX Spectrum –Pike spectrometer with a resolution of 4 cm^{-1} was used for this type of investigation. The investigated range was between 400 and 4000 cm^{-1}.

The EDX measurements have been used to reveal the mass transfer between the target and the substrate, on one hand, and, on the other hand to determine the Ca/P atomic ratio. The coatings thickness has been measured by quantitative optical microscopy on cross sections performed on deposited samples. The coatings adhesion has been determined by scratch test measurements.

3. Results and Discussion

X-ray diffraction diagrams present picks of the TiN, $ZrO_2Ca_xMg_y$, HAp phase (Fig. 1).



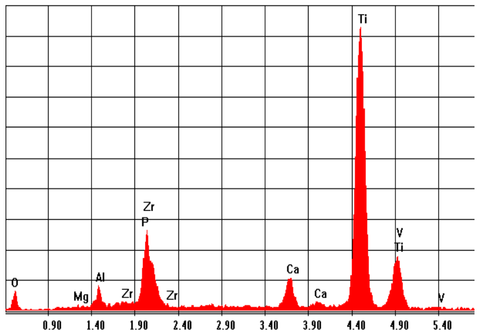
● - Titanium (ICDD: 44-1294); hexagonal
■ - Hydroxylapatite (ICDD: 9-432); hexagonal
❖ - Zirconia (ICDD: 49-1642); cubic
◆ - Rutile (ICDD: 21-1276); tetragonal
□ - Anatase (ICDD: 01-89-4203); tetragonal
▽ - Titanium Nitride (ICDD: 03-89-4203); cubic

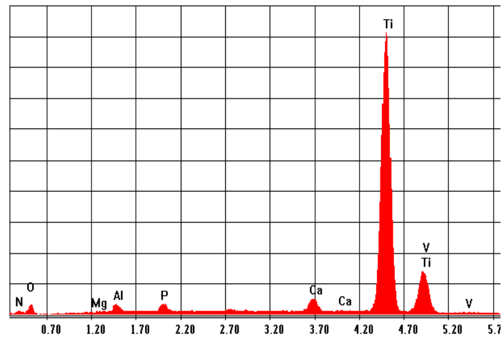
Fig. 1 XRD patterns of ZrO_2 /HAp and TiN/HAp coated Ti6Al4V alloy

The XRD analysis indicated a good crystallinity of the HAp coatings heated in air at 550^0C.

The chemical analysis performed by EDX has been used in order to determine the Ca/P molar ratio. The theoretical value of this ratio for a stoichiometric compound is 1.67. The EDX analysis performed on the deposited coatings indicated a mass transfer between the two coatings. The TiN intermediary coating acts as a diffusion barrier between the HAp and the substrate.

The results of the EDX measurements are presented in Fig. 2.





Element	Wt %	At %
O K	23.46	47.34
MgK	0.79	1.05
AlK	3.04	3.64
P K	4.96	5.17
ZrL	10.27	3.64
CaK	3.73	3
TiK	52.13	35.14
V K	1.61	1.02
Total	100	100

a

Element	Wt %	At %
N K	4.09	9.12
O K	20.49	39.98
MgK	0.21	0.27
AlK	1.78	2.06
P K	1.35	1.36
CaK	2.12	1.65
TiK	69.54	45.31
V K	0.41	0.25
Total	100	100

b

Fig.2 Results of the EDX of ZrO_2 /HAp (a) and TiN/HAp (b) coatings on Ti6Al4V alloy

The coatings have been also analyzed by FTIR (Fourier Transform Infrared Spectroscopy), the investigated wavelength range have been selected to that Fig. 3.

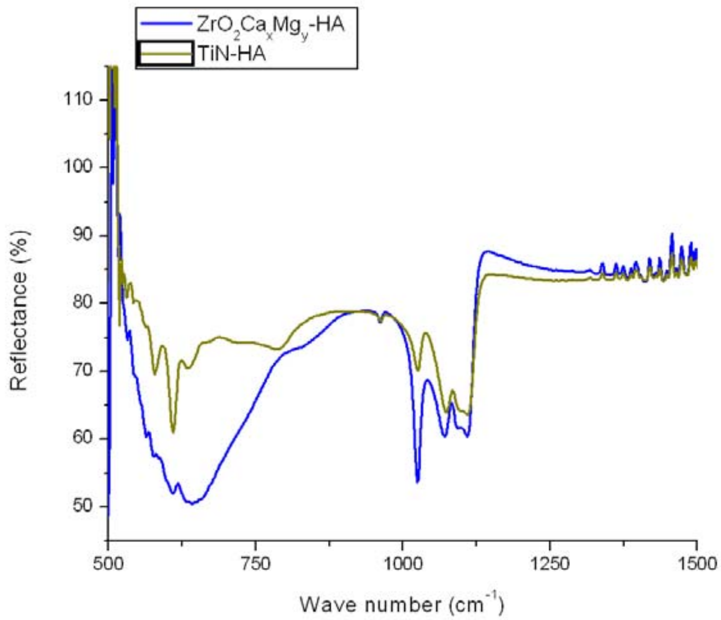


Fig. 3. FTIR spectra of coatings on Ti6Al4V alloy

- FTIR spectra showed vibration modes typical for hydroxiapatite with strong vibration features at 564, 578, 607, 960, 1024, 1073 and 1094–1115 cm^{-1} (phospatic) and 636 cm^{-1} (hydroxyl)
- The narrow width of the vibration corresponding to the phosphate and hydroxyl compound indicates a good crystallinity of the HAp coatings
- The spectra showed a wide distinctive band situated in the region 800 – 600 cm^{-1}. This band hasn't been observed in the spectrum corresponding to TiN-HAp coatings deposited without zirconia interlayer
- Based on previous observation, the band situated between 800 – 600 cm^{-1}, can be ascribed to either TiO_2 vibrations, due to a high oxidation of the substrate accompanied by a diffusion process within the coatings, or, to the ZrO_2 vibrations. This hypothesis has been discussed in the literature. It is known that most of the simple metallic oxides don't have any absorption band in the region 4000 – 650 cm^{-1}, but the oxides with more than one oxygen atom bonded to a metallic one can have a strong absorption in the region 1020-970 cm^{-1}. Generally metallic oxides of type M=O exhibit a strong absorption in the 1100-

825 cm^{-1} region, while some dioxides compounds can have this vibration band lower in the spectrum , at around 750 cm^{-1}.

The coatings thickness has been determined on cross sections by using quantitative optical microscopy. The thickness had an average value of 3.2 μm for the ZrO_2/HAp coating, while the average value of the TiN/HAp coating was 5.8μm. The adhesion measurements have been performed by scratch test. The critical load, corresponding to the detaching of the coatings is presented in the Table 3.

Table 3

The critical load

Sample	Fc [N]
ZrO_2/HAp	35-40
TiN/HAp	48-53

4. Conclusion

As shown by our experiments, RF magnetron sputtering is a promising technique for obtaining bioactive films. The adhesion of the films to the substrate and the growth of crystalline structures of the films are the predominant factors in determining the performance and reliability of dental and orthopaedic implant applications.

XRD and FTIR investigations have demonstrated that a heat treatment process applied after deposition leads to an increase of the crystalinity degree of the HAp coatings. The investigations showed that a mass transfer occurs between the two coatings. A TiN interlayer can represent a difussion barrier between HAp coatings and the substrate, on one hand, and, on the other hand, it can increase the adhesion of the coating to the substrate.

R E F E R E N C E S

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