RESEARCH ARTICLE

AUGER SPECTROMETRY AND X-RAY PHOTOELECTRON SPECTROSCOPY ANALYSIS OF TITANIUM COATING ON NaCl SUBSTRATE FOR DENTAL IMPLANT APPLICATIONS.

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Manuscript Info

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Abstract

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Titanium coatings were preparing on NaCl substrate using R.F. magnetron reactive sputtering in order to make chemical analysis for dental implant applications.

The analysis of the structure by electron microscope revelated that the titanium coating have "a" lattice constant related to the mode of deposition and the experimental conditions. The qualitative analysis by Auger Spectrometry and X-ray Photoelectron Spectroscopy (XPS) showed that the titanium dental films contained at least on the surface a large amount of carbon and oxygen. The increase of the lattice constant "c" for titanium was attributed to the incorporation of impurity atoms.

Any significative difference in grain size with respect to titanium deposits regardless of the deposit conditions was observed.

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Introduction:-

The use of titanium in dental implants has a great interest because of its biocompatibility with biological tissues[1]. Despite many studies carried out the cost of dental implants remains high[2]. To minimize this cost the thin titanium films were prepared on NaCl substrate.

In this perspective Auger Spectrometry and X-ray Photoelectron Spectroscopy (XPS) analysis have a great importance because it provides information on the physico-chemical properties of titanium[3,4,5].

In this work microscopic diffraction for films less than 1 micron, Auger spectrometry and X-ray spectroscopy (XPS) were used to analyze titanium dental films deposited on NaCl substrate using R.F. magnetron reactive sputtering technics.

Experimental details

The substrates on which the titanium is deposited is the NaCl. The NaCl was chosen because the film prepared on this substrate can easily be detached by simple dissolution in water. The NaCl crystallizes in a face-centered cubic system; the crystal parameter is a = $5,6402.10^{-10}$m.

The NaCl is previously cleaved in the open air before introducing it into the vacuum chamber.

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After introducing the sample, the vaccum chamber was pumped down to the total ambient pressure of $(5-7).10^{-4}$ Pa. The pressure in the vaccum chamber was raised to the desired value for deposition 7.10^{-1} Pa by introducing argon gas through a pressure valve. Some of samples were heated at given temperature during the deposition process. The others were coated at room temperature (RT) and subsequently heated at a given temperature, for a given time period. In every case, the samples were kept in the vaccum chamber until they had return to room temperature (RT). Under such circumstances, equal deposition times were used for all samples giving a coating thickness of about 500 nm.

Conditions for obtaining titanium films
Titanium films with hexagonal structure were prepared after looking for the conditions of suitable vacuum pressure. These conditions were obtained after degasing for three hours about 300 ° C of the enclosure and its constituents. For pressures lower than the limit pressure $1,33.10^{-4}$ Pa, the films have an abnormal structure, in this case they have a cubic centered-face structure (C.F.C).

Titanium film with thicknesses ranging from 6.10^{-8} m to 2.10^{-7} m were deposited by magnetron sputtering radiofrequency on NaCl substrate, under an argon plasma pressure of $6,65.10^{-1}$ Pa.
The radiofrequency power used is 900 W, which gives in the case of the magnetron RF a speed of 10^{-9} m/s. The temperature measured during the deposition was about 85°C for 6.10^{-8} m thick titanium films prepared on NaCl substrate.

Operating procedure for titanium deposits by cathodic magnetron RF Sputtering
The prepared NaCl substrate are fixed on a substrate holder in the vacuum chamber. When the pressure in the chamber reaches $1,33.10^{-5}$ Pa, argon is introduced up to the pressure of $6,65.10^{-3}$ Pa. By throttling the communication valve enclosure - diffusion pump, it is possible to reduce the pumping rate once the gases introduced into the chamber so as to achieve a stable pressure equilibrium. The plasma is then primed. Before any deposit, it is necessary to pre-spray (target cleaning phase) for about ten minutes. Meanwhile, the substrates are hidden to avoid polluting them.

After the cleaning of the target, a new pumping is carried out until a residual pressure of $1,33.10^{-5}$ Pa is obtained. Argon is again introduced under a pressure such that the plasma can be initiated. by adjusting the incident power to 900 W in the conditions of our experiments.

You can then adjust the total working pressure. In this experiment, the thermocouple is placed behind the NaCl substrates so as to determine his temperature during the deposition.

Titanium implants structure
The black background image is formed by the electrons contained in the diffracted beam. This is obtained by selecting with the selection diaphragm a point hkl of the diffraction diagram.

This technique allows to visualize the grains in different orientations making it possible to evaluate their size.
The diffraction pattern allows to determine samples orientation and their structure by their crystalline parameter.
According to the Ewald construction, the diffraction pattern is given by the cross of the reciprocal lattice by a perpendicular plane to the incident beam and passing through the origin of the reciprocal lattice. Only beams obeying the Bragg condition participate in the formation of the diffraction diagram.

The condition of Bragg is written:

$$2 d_{hkl} \sin \theta = \lambda \quad (1)$$

(d_{hkl} is the distance between the atomic planes hkl, λ is the wavelength of the electron beam).

If the sample to be analyzed is polycrystalline, the diffraction pattern is formed of rings, the measurement of the diameters of the rings allows us to determine d_{hkl} knowing that:

$$d_{hkl}D = 2\lambda L. \qquad\qquad (2)$$

(λL is a constant of the microscope, D the diameter of the ring).

We measured the diameters of the rings at the comparator using the pointer. The technique consists of scanning the diffraction rings with a diameter and measuring the diameter corresponding to the maximum of the intensity. The value chosen is the average of several measurements. By this method the measurement error is $0,02.10^{-3}$ m.

Titanium is hexagonal compact at temperature below 800 ° C. Its crystalline parameters are:
a $=2,950.10^{-10}$ m; c $=4,686.10^{-10}$ m

The distance $d_{hkl} = \dfrac{a}{\sqrt{\dfrac{4}{3}(h^2 + k^2 + hk) + \dfrac{l^2 a^2}{c^2}}} \qquad (3)$

Microscope constant determination λL:
This constant is determined using a gold thin film standard. This gold film is recovered on a microscopic grid bearing the titanium film. The diffraction pattern obtained shows both the rings of gold and titanium. The ring of gold which appear correspond to the plane (111), (200), (220), (311), (331). The measurement of the gold rings diameters that appear on the plate allowed us to determine for each observation. The error in the parameter measurements can be determined. Measuring diameters with an error of 0,02 mm allowed us to determine the crystalline mesh with an accuracy less than 1,5 ‰

Principle of the process Auger
Auger titanium peaks are observed at 382 eV and 418 eV. They correspond respectively to transitions $L_3M_{23}M_{23}$ and $L_3M_{23}M_{45}$ (Figure 1) and the kinetic energy of the Auger electron in each case is given by:

$$E_c = E_{L_3} - E_{M_{23}} - E_{M_{23}} - \phi \qquad (4)$$

and

$$E_c = E_{L_3} - E_{M_{23}} - E_{M_{45}} - \phi \qquad (5)$$

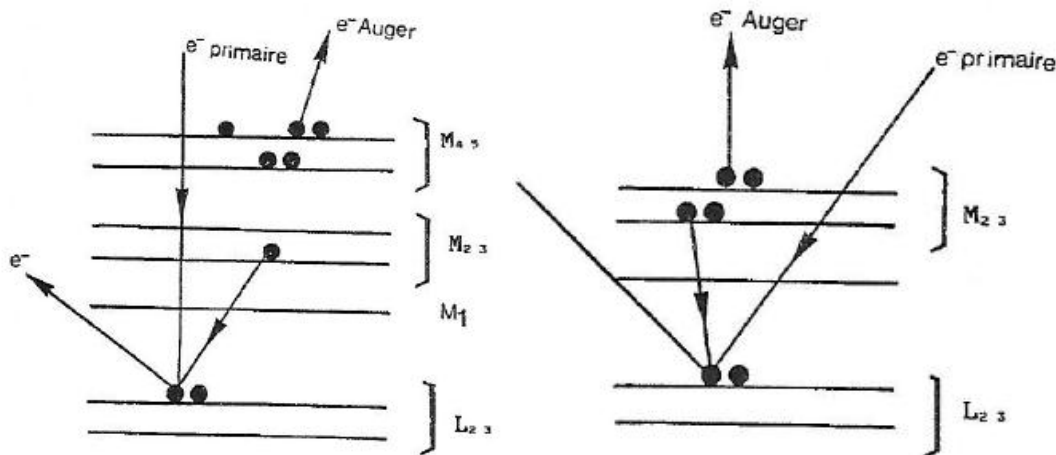denote the energies of the L and M_{23} levels.

Figure 1: -Transitions corresponding to titanium Auger peaks at 382 eV and 418 eV.

The Auger electron distribution N (E) can be recorded according to their kinetic energy E. The observed peaks then allow to identify the different elements present on the surface of the sample.

Often because of the low intensity of Auger electrons in N (E) the Auger peaks are difficult to observe. The function is then recorded $E\dfrac{dN(E)}{dE}$ to improve the sensitivity of the technique.

Results and discussion: -
Titanium implant structure
The electron microscopic analysis shows that the titanium films are continuous with grains whose average size is 6.10^{-9} m.

The diffraction patterns obtained on titanium films prepared on NaCl substrate is presented on figure 2. There is therefore no preferential orientation.

Measurement of ring diameters allowed us to determine the lattice distances according to Miller indices using the Bragg formula (2).

The formula (3) allowed us to calculate the crystalline parameters "a" and "c".
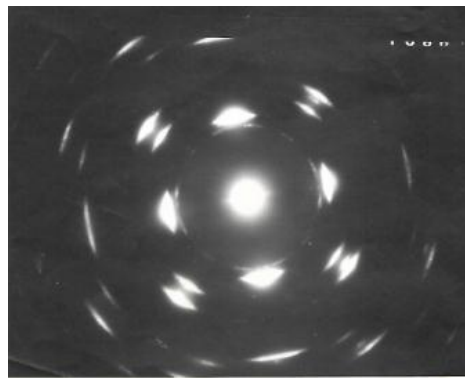

Figure 2:-Diffraction pattern of Ti / NaCl

Results obtained on parameters measurement are presented in table n ° 1. We note that for the prepared films, the parameter decreases with respect to the theoretical parameter, whereas the "c" parameter increases.
From the crystal lattice measurements, a dilatation of the lattice constant was observed.

Dépôt/ Support	e x 10^{-8}(m)	λLx10^{-13}(m^2)	d_{hkl} mesuré x10^{-3}(m)	hkl	ax10^{-10}(m) cx10^{-10}(m)	āx10^{-10}(m) čx10^{-10}(m)
Ti/NaCl	6	31,991	25,08	010	a = 2,945	ā = 2,934
			27,60	002	c = 4,636	č = 4,797
			28,21	011	c = 4,958	
			43,74	110	a = 2,924	

Table n°1: -Experimental lattice constant of titanium dental implant.

Observation of coating surface by Auger spectrometry.
Auger analyzes were performed with a primary energy of 3 KeV. It shows in general on surface the presence of carbon and oxygen. A spectrum obtained on a titanium film is shown (figure 2). It has a peak of carbon at 272 eV, two titanium peaks at 382 eV and 418 eV and then a peak of oxygen at 510 eV.
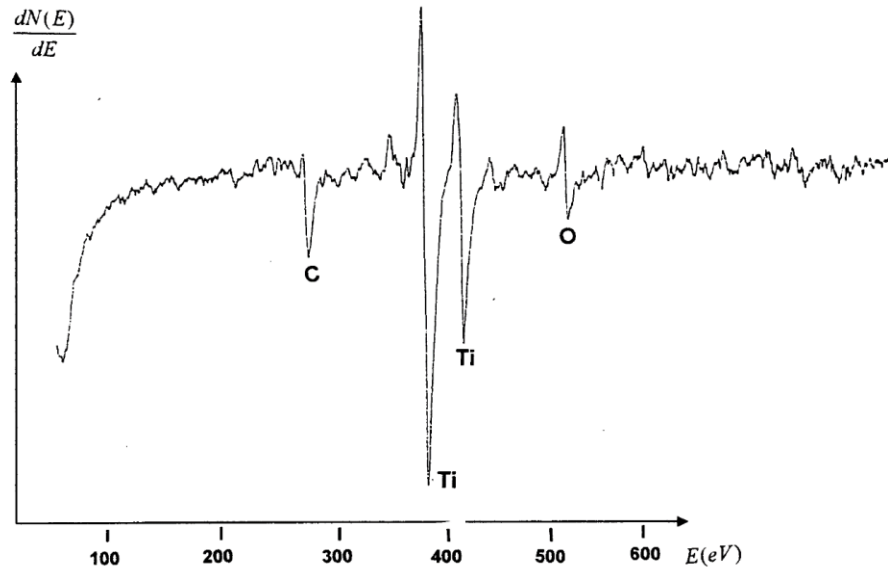
Figure 3: -Auger analysis of titanium implant films

X-ray photoelectron spectroscopy analysis.

For X-ray Photoelectron Spectroscopy (XPS) analyzes, photons X with energy hγ = 1486,6 eV were used. Figure 3 shows the spectrum obtained on a titanium film with a thickness of 2000 Å. Four titanium peaks 2s (568 eV), 2p (460 eV), 3s (60 eV), 3p (35 eV), two oxygen peaks 1s (534 eV) and 2s (21 eV) then a peak of carbon C_{1s} (287 eV) were observed.
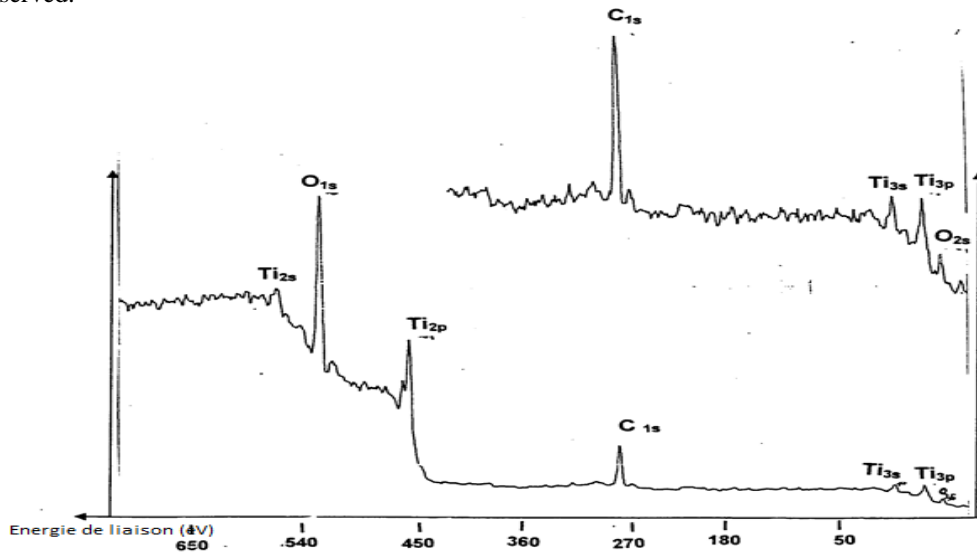

Figure 4: -XPS analysis of titanium implant films.

The Auger or XPS results showed that the titanium films are strongly contaminated on the surface by carbon and oxygen.

Given the high reactivity of titanium on oxygen, we can think that there is a surface film of oxide; which is related to the displacements of the oxygen peak (Ti 3p) in the XPS spectra of titanium.

Conclusion:-

In this work, the conditions of preparation to obtain titanium dental film having a normal hexagonal crystallographic structure were defined. This structure is not maintained if the vacuum conditions are not suitable, the incorporation of impurities producing a structure modification which becomes cubic with centered faces.

The qualitative analysis of the titanium films by Auger and XPS showed that the films contained at least a large amount of carbon and oxygen at the surface. The structure analysis using electron diffraction and X-ray revealed that the titanium dental films have a lattice parameter generally greater than the theoretical parameter whatever the experimental conditions. The increase of the parameter "c" for titanium was attributed to the incorporation of impurity atoms.

Any difference on grain size with respect to titanium deposits regardless of the experimental conditions was observed.

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