Physical characterization of nanostructured thin films used to improve hip prostheses

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Depositions of TiN thin films on SS 316L steel substrates by Pulsed Laser Deposition (PLD) method were realized to improve general performances and, in particular, mechanical characteristics of hip prostheses. The number of laser pulses applied varied between 5000 and 20000. Physical characterization of deposited thin films using Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD) and Atomic Force Microscopy (AFM) were performed in order to test the adhesion of the coating on the substrate. FTIR investigations have demonstrated the existence of a N-H bond and thus, stoichiometric transfer of the material. The achieved XRD diffraction patterns showed that TiN coatings were polycrystalline. The AFM system contributed to obtain some information referring to the surface of deposited layer, determining topographic parameters from ultraprecise measurements. From these studies of the authors, the conclusion was that the protective coating of TiN deposited by PLD technique is a suitable solution in order to improve characteristics of hip prostheses.

(Received March 24, 2014, accepted July 10, 2014)

Keywords: Hip prostheses, Thin films, Fourier Transform Infrared Spectroscopy, X-ray diffraction, Atomic force microscopy

1. Introduction

The hip prosthesis is a complex mechanical biotribosystem having the functions of guiding, coupling, motion stopping, energy transmission and power.

Under the action of the dynamic cyclic loadings and complex movements with six degrees of freedom, performed in a biologically adverse environment, the hip prostheses can lose their optimal functionality in time [1]. Thus, wear phenomena appear at the interface of systems components - acetabular cup and femoral head. This results in the deformation and wear of the acetabular cup, and the change in the roughness of the femoral head surface, the appearance of wear particles and their expulsion in synovial fluid, the appearance of the three-body wear. All these negative effects lead, finally, to the rejection of the prosthesis by the human body. The destruction of the structure of a hip prosthesis depends on the size and volume of the particles and on their total volume or on the type of the material. Practically, the material is not perfectly smooth, and without any roughness. At these pre-existent roughnesses of the materials, the wear is added in natural systems, generating osseous or prosthetic high roughness surfaces.

Over time many studies of prosthetic systems were achieved to observe their evolution during the use after the implantation in the human body. From all clinical and theoretical studies that were conducted, a need to achieve a resistant prosthesis, with anticorrosive composition and high mechanical properties, was noticed. Gradually, in order to improve the mechanical properties of the prosthesis, these ones were made of different materials, and were processed or coated with different higher quality materials. Each material has a different microstructure and, therefore, different properties, optimized for a specific design or function. The composition and microstructure of the alloy affect the corrosion behaviour of the body fluids, due to changes in surface chemistry. Improvement of tribological performances, through constructive changes and even of the operation principle, was intended.

In this project we attempted to find some solutions for these shortcomings. Thin films depositions (nanomaterials) on cylindrical samples of steel SS 316L were achieved to increase friction resistance.

2. Experimental Materials and Methods

In order to improve the principal performances and, in particular, mechanical characteristics of hip prostheses structures, thin films of titanium nitride (TiN) were deposited on SS 316L steel substrates.

Because of the lack of appropriate technical and technological advanced means for deposition of TiN coatings on spherical surfaces, we assumed that the friction thimble femoral head/ acetabular cup would have an infinite radius at the limit. In this situation, the femoral head could be modeled by a flat metal surface, represented by cylindrical samples.

TiN depositions were achieved by physical laser deposition (PLD) method inside a deposition chamber, with stainless steel reaction chamber at 5000, 10000 and 20000 pulses.

TiN commercial tablets from Plasmaterials (99.5% purity, 1" diameter x 0.250" thickness) were used as targets for experiments, while disks made of SS 316L

stainless steel (22.5 mm diameter and 10 mm height), with hardness of 150 HV_{30} were used as substrates for deposition. The surfaces of the substrate samples were polished with increasing granulation sand paper, from 200, 400, 600 up to 800, and then polished mirror on felt with diamond paste.

Disk samples were placed in parallel with the targets (on geometric axis), at a 5 cm distance, in front of them. The laser fluency on the target surface was ~ 4.8 J/cm^2, at an energy of 500 mJ. Before the deposition, in order to eliminate the microimpurities, the targets umderwent a cleaning process [2] with 1000 laser pulses. During this procedure, a shutter was inserted, between the target and the substrate, in order to collect the flow of expelled impurities and flaws. During the deposition, the substrates were heated and maintained at a constant temperature (500°C) using a PID-EXCEL temperature controller.

All coatings were made in a dynamic flow of N_2 constantly controlled by a MKS 400 mass flow controller. The pressure inside the deposition chamber was ~ $2x10^{-3}$ Torr and the number of consecutive laser pulses varied from 5000 up to 20000 pulses.

Deposited layers were physically characterized by the intelligent mechatronic systems and technologies – Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD) and Atomic Force Microscopy (AFM).

Fourier Transform Infrared Spectroscopy (FTIR) represents a non-destructive analytical technique and technology, that was used to determine the nearby order, of the IR vibration modes, identification of chemical bonds and functional groups, and emphasize the nature of the structures chemically increased in vitro.

IR spectroscopy represents a technique and technology of quick and simple chemical analysis, and it is based on the interaction between the electromagnetic radiation with the molecules. This technique is sensitive to the presence of the functional chemical groups from a sample, thus allowing the use and the identification of the structural fragments of the molecules.

The most intense features found in the IR spectra can be attributed to the fundamental transitions of the molecules, and the correlation between these bands and the chemical structure represents the basis of IR spectroscopy, making of this an important instrument for the chemical analyses. In order to identify unknown molecules from IR spectra, few characteristics of the absorption bands (such as, for example, the position, intensity and width at half of maximum) must be taken into account.

FTIR investigations were carried out on a mechatronic device equipped with an infrared microscope, in a single optical phase, in a wavelength range of (7800-350) cm^{-1}. The investigations were carried out both in the 10Spec geometry and in the 80Spec geometry. The 10Spec device disposes of a collimated beam that strikes the sample at an incidence angle of 10 degrees. 80Spec technology that was used, is an enhancement with 80 degrees regular reflexion.

The microstructure of TiN coatings deposited by PLD was investigated using X-ray diffraction technique and technology.

Diffraction measurements were performed with CuKα radiation on a system equipped with parallel optics and θ-θ vertical goniometer.

The divergence angle of the beam emitted by the multilayer mirror is approximately 0.05^0. This optics type is suitable for thin films analysis, particularly for the measurements of the residual stresses, due to the strong intensity of the beam and of the significant reduction of the instrumental errors (the position of the diffraction lines is not out of phase, the shape and the width of the diffraction lines profiles is maintained even at large angles of inclination) [3].

Grazing Incidence X-Ray Diffraction (GIXRD) technique and technology were used to obtain diffraction patterns. Using a small angle of incidence, this technique enabled to get the information from a small volume adjacent to the sample surface, the intensity diffracted by the analyzed layer is greater than in the case of the conventional techniques (the influence of the substrate is reduced). Also, a very important aspect for the analysis of the states stresses in films is that the investigated depth stays relatively constant over the entire analysis range.

X-ray diffraction patterns were acquired at a fix angle of incidence $\alpha = 1^0$, in the angular range 2θ of $340\text{-}105^0$, with acquisition step of 0.02^0 and counting time per step of 10s.

Microstructural analysis was performed by the use of a specialized software package that allows to analyze the full diffraction spectrum. Pseudo-Voigt TCH function [4] including Finger correction of the axial divergence [5] was used for modelling the physical profile.

Precise investigations were made by means of the intelligent mechatronic system – atomic force microscopy (AFM).

The investigation procedure by means of the intelligent mechatronic system - AFM consisted in identifying and photographing of a damaged area with the surface of 50 x 50 μm. This area was divided into fragments, for each area and fragment were performed 3D records of the state of surface topography, being automatically recorded at the same time the surface topography parameters as well: minimum and maximum height of asperities h_{max}, average roughness S_a (R_a), total roughness S_y (R_y), ten points height S_z (R_Z), the root mean square S_q (R_q), surface skewness S_{sk} (R_{sk}) coefficient of kurtosis S_{ka} (R_{ka}) and other parameters.

The surface skewness S_{sk} (R_{sk}) assesses the asymmetry degree of a distribution and characterizes, along with the coefficient of kurtosis S_{ka} (R_{ka}), the shape of the distribution (illustrated as histogram). The surface skewness S_{sk} (R_{sk}) is negative or positive according if sampling distribution is asymmetric to the left or, to the right, respectively. A symmetrical distribution, such as normal distribution, has zero asymmetry.

The coefficient of kurtosis S_{ka} (R_{ka}) is part of the assessment indices of a distribution form. A high coefficient of kurtosis indicates a distribution with large "tails" (present categories spaced apart from the mean), while a small coefficient of kurtosis shows a distribution in which fewer categories away from the mean are presented. In the case of a distribution close to normal distribution, the coefficient of kurtosis is approximately 3. Based on this result, the excess E is defined as the difference between the coefficient of kurtosis and 3. For E > 0, the distribution is called leptokurtic (the height of the curve is higher than the normal one), and for E < 0, it is called platikurtic (the curve is flattened). If E = 0, the distribution is mesokurtic. The data sets with large excess tend to have a distinct peak near the mean. The data sets with low excess tend to have a flat maximum near the mean, rather than a sharp peak. A uniform distribution would be the extreme.

3. Experimental results

Layers with different thickness were obtained depending on the number of laser pulses applied.

3.1 Investigation of diffusion through advanced technology – Fourier Transform Infrared Spectroscopy (FTIR)

TiN layers deposited on SS316L stainless steel disks were investigated with FTIR technique in 10SPEC geometry and 80SPEC geometry. Figs. 1 and 2 present the FTIR recordings of the TiN target and of the thin films deposited, in 80SPEC geometry, respectively, 10SPEC geometry.

The use of the advanced technology - FTIR spectroscopy - may prove the molecular vibration modes that belong to the main functional groups or it can determine the nature of the chemical bonds. Spectrum matches identify the constituents in the sample. Most molecules present functional groups that absorb radiation from the IR middle region, which is found between 4000 and 400 cm^{-1}. Generally, the absorption bands, in the range of 1500–4000 cm^{-1}, are typically due to the functional groups (e.g. –OH, C=O, N–H, CH_3, etc.). The absorption bands of 400–1500 cm^{-1} are generally due to inter-molecular phenomena and they are highly specific to each material.

In fig. 1 (80 SPEC geometry) one can observe similar signals of intensity depending on the wavelength, between the target sample and those of the coatings made with 5000 pulses (5k), 10000 pulses (10k), 15000 pulses (15k) and 20000 pulses (20k). An increasing change of the signal, around the value of 2500 cm^{-1}, 2360,949 cm^{-1} respectively, is observed with the increase of pulse number.

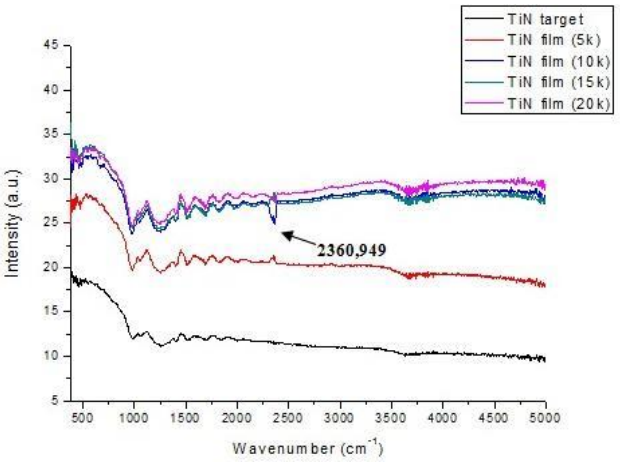

Fig. 1. FTIR of TiN target and deposited thin films (80 SPEC).

A similar phenomenon is seen in fig. 2 (10SPEC geometry). The difference from the first image is that an increased similarity of the signals is mainly observed for samples coated at 10000 pulses (10k), 15000 pulses (15k) and 20000 pulses (20k). Change of the signal appears around the value of 2500 cm^{-1}, namely 2362.773 cm^{-1}. A change of the signal at the value of 667.616 cm^{-1}, for samples with deposition higher than 10000 pulses (10k), is also shown in this diagram. This could be due to the existence of an intermolecular phenomenon.

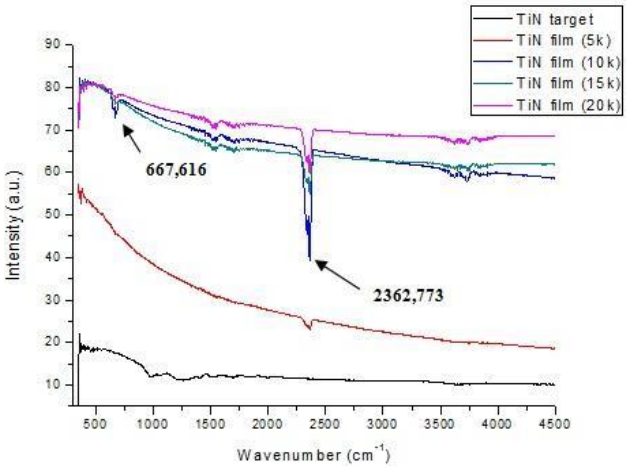

Fig. 2. FTIR of TiN target and deposited thin films (10 SPEC).

Following the performed FTIR investigations, absorption bands can be observed in the range 1500-4000 cm^{-1}, which demonstrates the existance of a N-H bond. Thus, this analysis demonstrates the stoichiometric transfer of the material, and the deposition of the TiN layer, respectively.

The presented graphs indicate the adhesion between coating and substrate through a diffusion layer in the depth of the base material.

3.2 Phase analysis and microstructural analysis by the advanced technique of X-ray diffraction

3.2.1 Phase analysis

X-ray diffraction patterns measured at a fixed incidence angle $\alpha = 1^{\circ}$ are presented in figs. 3 – 6. The qualitative phase analysis of the TiN coatings showed the presence of three polycrystalline phases in the analyzed samples:

- in the 5k and 10k samples – TiN (B1 cubic structure), Fe_{α} (cubic structure) and Fe_3O_4 (cubic structure).
- in the 15k and 20k samples – TiN (B1 cubic structure), Fe_{α} (cubic structure).

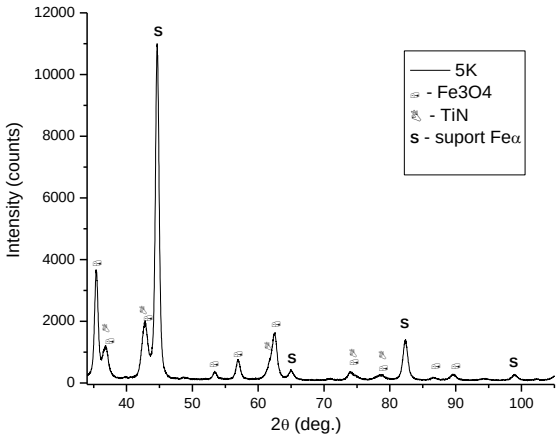

Fig. 3. X-ray diffraction pattern of 5k sample – phase analysis.

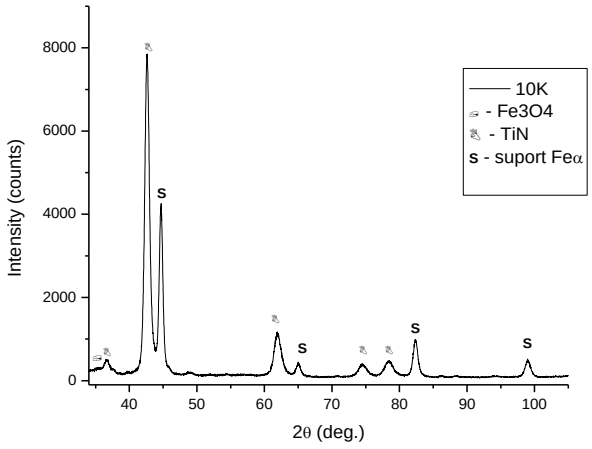

Fig. 4. X-ray diffraction pattern of 10k sample – phase analysis.

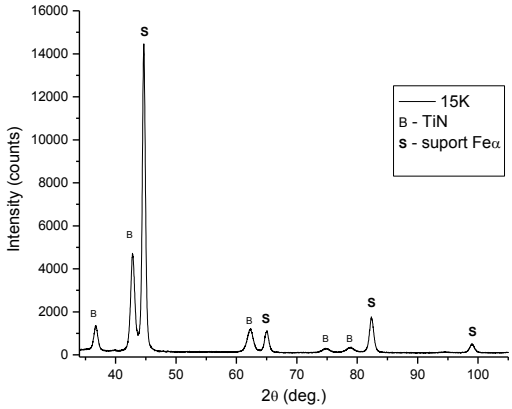

Fig. 5. X-ray diffraction pattern of 15k sample – phase analysis.

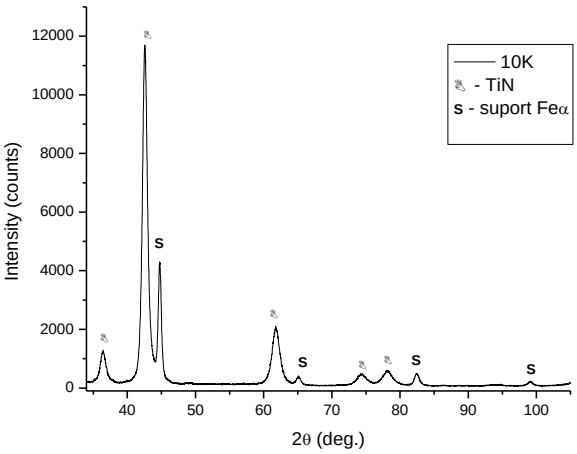

Fig. 6. X-ray diffraction pattern of 20k sample – phase analysis.

3.2.2 Microstructural analysis

Microstructural analysis was performed by the use of a specialized software package that allows Rietveld of the full diffraction spectrum analysis. Pseudo-Voigt TCH function that includes Finger correction of the axial divergence was used for modeling the physical profile.

The microstructural parameters, resulted from Rietveld analysis, are presented in table 1.

Table 1. Synthesis of the main parameters obtained from Rietveld analysis.

Sample code	Average size of crystallite (Å)	Average maximum microstrain (%)
5k	143.04	84.1698
10k	195.19	80.1921
15k	344.92	79.1179
20k	107.12	102.9714

3.3 Investigations of the TiN layers surfaces using the advanced technology – Atomic Force Microscopy

The advanced technology – Atomic Force Microscopy – was used for a complete characterization of TiN layers deposited with a particular number of pulses. Some examples of the TiN layers surfaces scanned using AFM are presented in fig. 7.

The TiN layer deposited at 5000 pulses has a surface with a lower uniformity, which could be the result of the more pronounced irregularity of the substrate. These results can be observed in fig. 7(a), after 2D scanning, and conversion of this image in 3D.

Topographic parameters determined (roughness, maximum height, ten points height, surface skewness, coefficient of kurtosis) provide information about the distribution of the deposited layer.

The surface fragments of the TiN layer deposited at 5000 pulses present positive symmetry indices, some with values close to zero. The existence of these positive values demonstrates that the distribution is asymmetric to the right.

The coefficient of kurtosis is part of assessment indices of a distribution form. After the analysis of these values, it was observed that the obtained excess values are both positive and negative, indicating a leptokurbic distribution (the height of the curve is higher than the normal one) and platikurbic (the curve is flattened). Most of these values are close to zero demonstrating an almost flattened uniformity.

The values of the surface roughness differ relatively little from one area to another, so that for TiN layer deposited at 5000 pulses, the mean value of the arithmetic mean roughness, obtained from these measurements, is 40,013 nm.

The surface of TiN layer deposited at 10000 pulses has a higher uniformity than that of the layer deposited at 5000 pulses. These results can be seen in fig. 7(b), after 2D scanning and conversion of this image in 3D. In these images, small surface flaws can be noticed, but their size is reduced.

The asymmetry index of this coating has, generally, negative values, but there are also positive values. This demonstrates that the TiN layer, deposited at 10000 pulses, has a probing distribution of the heights asymmetric to the left, but also to the right. Most of values are close to zero, which indicates that the distributions from the mass cases, are slightly asymmetric.

After obtaining the coefficient of kurtosis of the TiN layer deposited at 10000 pulses, one can notice that values of excess are both positive and negative. This indicates a leptocurbic distribution and a platicurbic distribution. The majority of these values are close to zero demonstrating an almost flattened uniformity.

The average value of the surface of the TiN layer deposited at 10000 pulses is 26.334 nm.

The surface of the TiN layer deposited at 20000 pulses has the highest uniformity from the 3 achieved samples (5000 pulses, 10000 pulses and 20000 pulses). This can be noticed from the 2D images of AFM scanning and conversion of this image in 3D (fig. 7(c)).

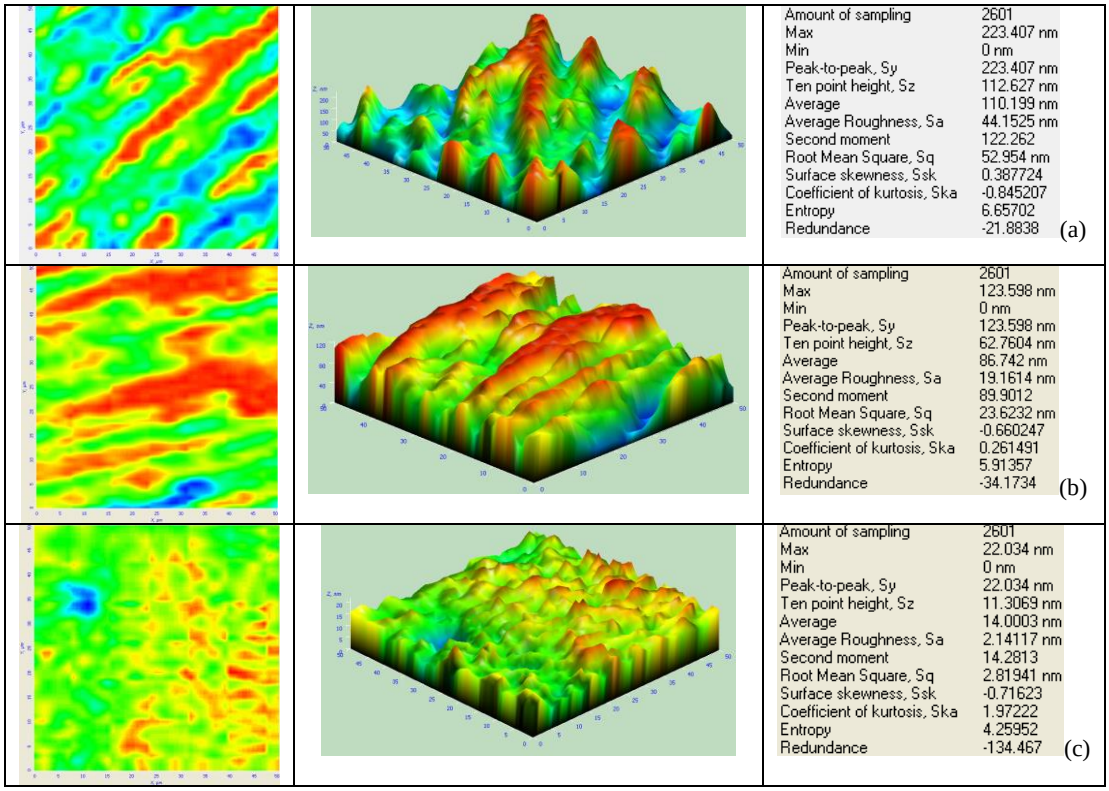

Fig. 7. AFM characterization and topographic parameters' values of the surface of the TiN layer deposited at (a) 5000 pulses, (b) 10000 pulses and (c) 20000 pulses.

Asymmetry index for the TiN layer has mainly negative, but also positive values. This demonstrates that the TiN layer deposited at 20000 pulses has an asymmetric distribution probe to the right, but also to the left. All the values of this index are close to zero, which indicates that the distributions from the presented cases are slightly asymmetric.

Both positive and negative values of the excess were obtained for the TiN layer deposited at 20000 pulses, starting from the coefficient of kurtosis. This result indicates a leptocurbic distribution and a platicurbic distribution. Most of these values are close to zero demonstrating an almost flattened uniformity.

Mean value of the roughness of the layer deposited at 20000 pulses is 2,527 nm. It is the lowest value of the mean roughness of the layer from these samples, which is also proved by the uniformity of surface coating, visible from AFM scanning.

It was observed that the values of the layers roughness vary function of the number of pulses at which the coating was deposited (40,013 nm for the sample with 5000 pulses; 26,334 nm for the sample with 10000 pulses; 2,527 nm for the sample with 20000 pulses). One can notice the decrease of roughness value with the increase of pulses number (fig. 8).

Considering that also the thickness of the layer increased with the number of pulses and considering that the surface of the substrate showed some minor flaws, it could be concluded that the layer became more and more uniform along with the more complete coating of initial flaws.

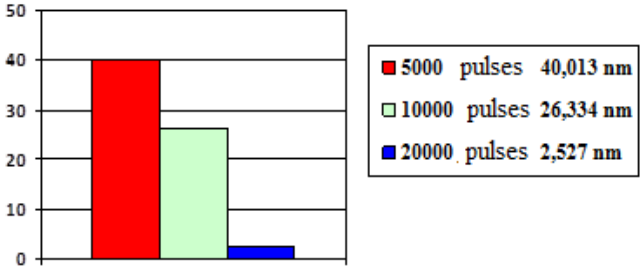

Fig. 8. Variation of mean roughness R_a (nm) of the TiN layer deposited depending on the number of pulses used in the process.

4. Conclusions

In the experimental attempts to obtain a proper solution to improve the quality of hip prostheses, TiN thin films were deposited on substrates of steel SS 316L. These were physically and tribologically tested and characterized.

High-tech FTIR investigations demonstrated the existence of a N-H bond, and thus, it may prove the stoichiometric transfer of the material, the deposition of the TiN layer, respectively. The graphs obtained and presented in the paper indicated the adhesion between the coating and the substrate by a diffusion layer in the depth of the base material.

XRD diffractograms, as adequate mechatronic intelligent systems, showed that the TiN coatings were polycrystalline, presenting reflexions assigned to the B1 cubic structure of TiN. Reflexions corresponding to the substrate (phase Fe_α) were detected in all X-ray diffraction models. In addition, the Fe_3O_4 polycrystalline phase was present in the 5000 and 10000 pulses samples.

The surface topography parameters, such as the minimum and the maximum height, average roughness, surface skewness, were determined using the AFM advanced technology resulting that there was a more veiled area under coating.

The roughness was used as an indicator of the deterioration in order to obtain information about the variation in height from one point to another.

After these studies, and other additional ones conducted in time (and presented in other publications – [6-8]), we consider that the protective coating of TiN deposited by PLD technique is a solution for the improvement of the characteristics of hip prostheses.

Acknowledgements

The authors thank Prof. Dr. Ion Mihailescu from National Institute for Laser, Plasma and Radiation Physics, Laser-Surface-Plasma Interactions Laboratory and Sorin Moga, Denis Negrea from the University of Pitesti, Research Center for Advanced Materials for their help in realizing deposition of TiN films and characterization using X-ray diffraction technique.

References

[1] M. Popescu, L. Capitanu, Total hip prostheses. Orthopaedics and engineering, Bren Publishing House, Bucharest (2006)
[2] G. Socol, A.C. Galca, C.R. Luculescu, A. Stanculescu, M. Socol, N. Stefan, E. Axente, L. Duta, C.M. Mihailescu, V. Craciun, D. Craciun, V. Sava, I.N. Mihailescu, Digest J. Nanomat. and Biostr., **6** (1), 107 (2011).
[3] A. Kumar, U. Welzel, E.J. Mittemeijer, Z. Kristallographie Suppl. **23**, 55 (2006).
[4] P. Thompson, D.E. Cox, J.B. Hastings, J. Appl. Cryst. **20**, 79 (1987).
[5] L.W. Finger, J. Appl. Cryst. **31**, 111 (1998).
[6] Gh.I. Gheorghe, L.L. Badita, Adv. Mat. Res. **741**, 67 (2013)
[7] L.L. Badita, Gh. Gheorghe, Adv. Mat. Res., **837**, 675 (2013)
[8] L.L Badita, Gh. Gheorghe, Digest J. Nanomat. and Biostr. **8** (1), 53 (2013).

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