

A Modified Laser Deposition Technique for Depositing Titania Nanoparticles on Commercially Pure Titanium Substrates (Mechanical Evaluation)

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ABSTRACT: Background: The nanostructured Titania coatings have been specifically used to improve titanium dental implant surfaces. However, the using of different deposition techniques and parameters can provide different Titania film properties. The aim of the study is to evaluate the nanostructured Titania films deposited by a modified laser deposition technique on the commercial pure titanium substrates, which are the most widely used material in orthopedic and dental implants.

Materials and methods: Grade (2) commercial pure Titanium sheets and discs, were used as substrates for depositing Titania nanoparticles by a modified laser deposition technique. The produced films are then evaluated by using XRD, micro - morphological analysis, AFM, microhardness values, SEM, film thickness measurements and EDX investigations.

Results: Depositing Titania nanoparticles films by the modified laser technique provides very thin films with different micro and nano-morphological properties on the titanium substrate; this either by changing of the type nanoparticle suspension or the used laser parameters. An improvement in the surface microhardness values were also resulted in comparison with uncoated titanium samples.

Conclusion: The modified laser deposition technique can be used as a simple, quick, low cost and highly efficient technique to deposit high quality thin metal oxide nanoparticles films on titanium surface. However, this modified technique can provide controllable coating film properties to accommodate the needs of different applications; such as to modify the surfaces of orthopedic and dental implants with metal oxide nanoparticles to improve their mechanical and biological properties.

KEYWORDS: modified laser deposition, Titania coatings, thin films, titanium substrate.

I. INTRODUCTION

Titanium and titanium alloys have been used widely for several decades as a material of choice for medical devices including orthopedic and dental implants⁽¹⁾. Because of its ability to interact intimately with bone tissue, CP Ti is widely used as a dental implant material under load bearing conditions, even this interaction does not involve a chemical bond with bone. In addition, it is considered to be the best biocompatible metallic material as a result of the spontaneous build-up of an inert and stable oxide surface layer^(2,3).

For decades, great efforts have been made by using various coating techniques to produce and improve the titanium surface oxide film to achieve better biological response of Titanium-based dental implants. Each technique can produce Titania film with different thickness, chemical composition, surface morphology, crystallinity, pore configuration, and

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surface roughness. However, it is not clear whether these oxide properties can affect the bone tissue response separately or synergistically^(4,5).

The application of laser is considered an effective procedure for depositing films from nanoparticles on the metal substrates, this can be done by using several techniques such as laser cladding techniques, laser pyrolysis technique, laser assisted atmospheric chemical vapor deposition (CVD) and pulsed laser deposition (PLD). In spite of the proved mechanical effectiveness of the laser deposition techniques, many limitations were found in comparison with conventional coating techniques; such as their higher cost, time consuming, multiple step process needed, difficulties and limitations in application of coatings on complex geometries as well as small sizes substrates, drawbacks of predeposition and codeposition of coating nanoparticles in beam-material interaction zone and finally the use of binders that can cause imperfection of coating films such as porosity and cracks^(6, 7, 8).

In order to overcome the previously mentioned limitations, a modified laser deposition technique was used, in this work, for depositing Titania nanoparticles to produce several coating films on the titanium substrates. After micro and nano morphological comparison of these films, the most appropriate nanoparticle suspension and laser parameters have been determined to be used for future coating of titanium dental implant with titania film. This film was also compared morphologically, compositionally and mechanically with uncoated titanium substrates.

II. MATERIALS AND METHODS

A- SAMPLE PREPARATION

Commercial pure Titanium (grade 2) sheets, mirror polished from the source, were used as the substrate for coating. These sheets were cut by a sharp scissors into small rectangular specimens with the (35×12×0.25) mm dimensions. For micro-hardness test, a rod (32 mm in diameter) of commercial pure Titanium (grade 2), was used to prepare substrates for coating. The titanium was cut into small circular discs (32 mm diameter and 2 mm thickness) by lathe machine. Silicon carbide papers were used to polish the specimens to form uniform smooth surfaces. By using ultrasonic cleaning device, ultrasonic bath of ethanol absolute ($\geq 99.8\%$) was used to remove the debris and contamination from all substrates. This process was performed for about 15 minutes, then for 10 minutes in distilled water bath. Finally, the specimens were left to dry at room temperature.

B- SUSPENSIONS PREPARATION

For using Nanomaterials to produce coating films, it is desirable that the nanoparticles are dispersed into a liquid solution and also to be remain stable in that solution for a certain period of time. This because the controlling of the dispersion and aggregation of the nanoparticles is crucial to exploit the advantages of the nanometer- sized particles. Therefore, producing suspensions is necessary for the incorporation of nanoparticles in the liquid phase, the break up and dispersion of nanoparticle clusters, and subsequently stabilization⁽⁹⁾. In this work, titanium dioxide nanoparticles (TiO₂, Nanoshel LLC, USA) were used to prepare many suspensions by using polyelectrolyte dispersants (poly acrylic acid), distilled water or Micellar medium (Sodium dodecyl sulfate). Each suspension was used to coat the samples to select the best one for the laser deposition technique.

C- LASER WAVELENGTH SELECTION

The scan spectrum absorption curves of the prepared titanium dioxide nanoparticle suspensions were produced by using (UV-Vis-NIR) double beam automatic scanning spectrophotometer. The position of absorption peak spectra was located to determine the approximate range of wavelengths of the laser that can be used for best coating results. All suspensions appeared to have a peak spectra located within approximate wavelengths range of (Nd: YAG) laser at (1064 nm) and its (SHG) at (532 nm). Therefore and to select the most appropriate one to coat the final samples, these wavelengths were used in the coating procedure in the pilot study. The scan spectrum absorption curve for the final selected titanium dioxide nanoparticle suspension (distilled water) to be used for the deposition procedure is shown in (figure 1).

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Figure 1: Scan spectrum absorption curve of the titanium dioxide nanoparticle suspension (distilled water).

By using laser technique to produce titanium oxide coating films on the samples, the samples were completely immersed in a newly prepared titanium dioxide suspension. In a glass petri dish, the samples were covered with suspension of about (3) mm depth. Then were put in a fixed distance of (10) cm from the laser source; which is the focal length of the built-in lens and were irradiated by using Nd: YAG laser under the using of fixed laser parameters; with wavelength (1064) nm, energy (1000) mJ, pulse duration (10) n sec and pulse repetition rate (3) Hz.

After the samples were coated by laser within each suspension, the coating films properties were examined by both optical microscope (Olympus BX51M, USA), (figure 2), and atomic force microscope (AA3000 Angstrom Advanced Inc., USA), (figures 3, 4 and 5), to select the most effective suspension that can produce better Titania film. The best film in which coatings have better uniformity and distribution results, according to optical microscope and AFM results, were produced by using distilled water-nanoparticles suspension. However, these nanoparticles appear to have very good dispersibility in distilled water.

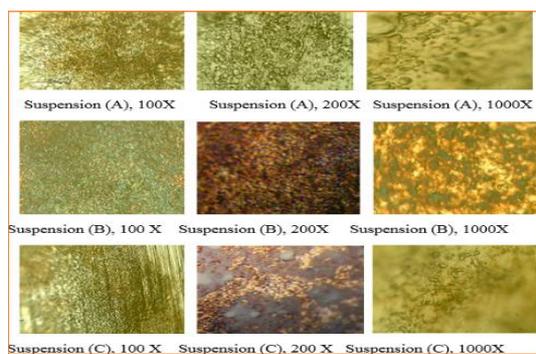


Figure 2: Optical micrograph (100X, 200X and 1000X) of coated samples by using (A- poly acrylic acid, B- distilled water and C- Sodium dodecyl sulfate suspensions).

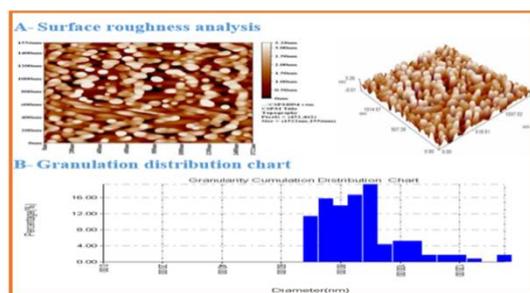


Figure 3: A- Surface roughness analysis, B- Granulation distribution chart. Of coated samples by using poly acrylic acid suspension.

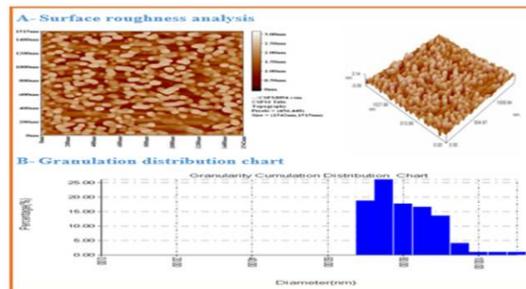


Figure 4: A- Surface roughness analysis, B- Granulation distribution chart. Of coated samples by using distilled water suspension.

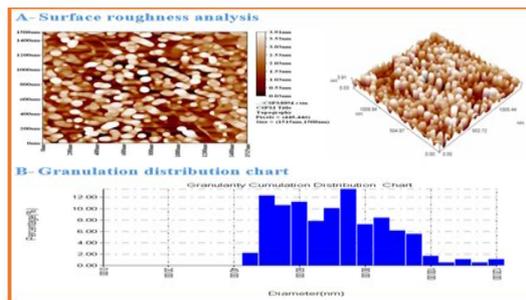


Figure 5: A- Surface roughness analysis, B- Granulation distribution chart. Of coated samples by using sodium dodecyl sulfate suspension.

D- SELECTION PULSE REPETITION RATE OF LASER

Almost the same previous Nd: YAG laser parameters (except the increasing of pulse repetition rate from (3) to (6) Hz) were used to coat the substrates to study their effects on the Titania film properties (from distilled water suspension). However, the results showed that the increase in pulse repetition rate had produced more uniform surface of the coating film with better particles distribution; according to optical microscope and AFM granulation distribution charts (figures 6 and 7). As well as the better surface roughness (which is preferable to improve implant surface). Therefore, the (6) Hz pulse repetition was selected as one of the laser parameters to be used to coat the final samples.

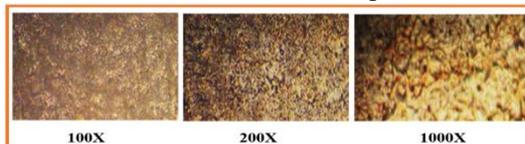


Figure 6: Optical micrograph (100X, 200X and 1000X) of coated samples by using Nd: YAG laser with pulse repetition rate (6) Hz.

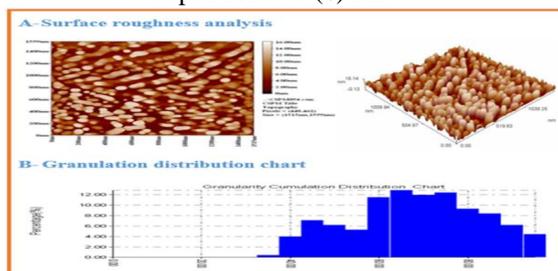


Figure 7: A- Surface roughness analysis, B- Granulation distribution chart. Of coated samples by using Nd: YAG laser with pulse repetition rate (6) Hz.

E- SELECTION OF LASER TYPE:

The coating film properties produced by (1064 nmNd: YAG laser, as showed infigure 6, 7), were compared with the film properties, (figure 8, 9), produced by green laser (532 nm) with the same previously used fixed parameters, to select the most effective laser type that can produce better titania film. However, it can be observed (according to optical microscope and AFM results) that Nd: YAG laser of (1064 nm) can provide more uniform surface of the coating film with an increase in the surface roughness and better granulation distribution. Therefore, Nd: YAG laser (1064 nm) was selected to coat titanium samples for final coatingcharacterization.

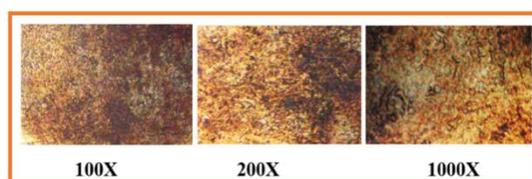


Figure 8: Optical micrograph (100X, 200X and 1000X) of coated samples by using Green laser with wavelength (532) nm.

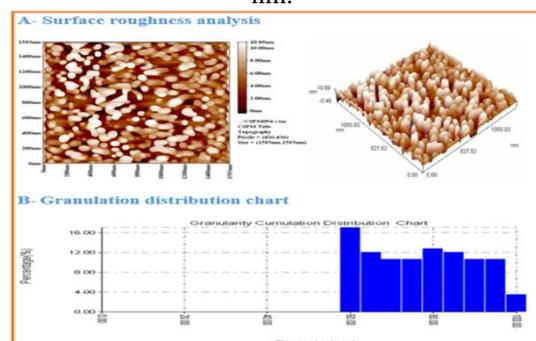


Figure 9: A- Surface roughness analysis, B- Granulation distribution chart. Ofcoated samples by using Green laser with wavelength (532) nm.

F- COATING CHARACTERIZATION

In addition to the previously mentionedmicro-morphological and AFM analysis,further specific characterizationfor the finally produced coating film; deposited by the selected suspension and laser parameters, were investigated.Howeverand after the gold ion sputtering of the coated samples by using an Ion sputter (ABC-12 Angstrom Advanced Inc., USA), the coating layers were evaluated for nano- morphological surface analysis and film thickness by using the Scanning Electron Microscope (SEM, AIS2300C Angstrom Advanced Inc., USA).For X-Ray phase analysis, the coating films were also investigatedby using XRD machine(Shimadzu Lab XRD - 6000, Japan).Themicrohardness valueswere also measured bymicro-hardness tester(INNOVATEST Europe BV, Netherlands). Moreover, the coating film material characterizationwas investigated by usingEnergy-Dispersive X-ray spectroscopy (EDX) analysis. Finally,all thefindings of these testswere compared with those of uncoated ones (controls).

III. RESULTS

A. NANO- MORPHOLOGICAL SURFACE ANALYSIS

Nano- morphological surface analysis of SEM images were evaluated foruncoatedsamplesand the nano- Titania coated ones. The results are shown in (figures 10, 11). Moreover and as measured by using the SEM, the coating films thickness wereabout (1-2) micrometers.

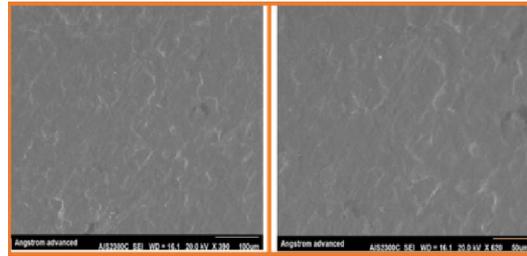


Figure 10: SEM of uncoated cpTi sample by different magnifications (100µm, 50µm)

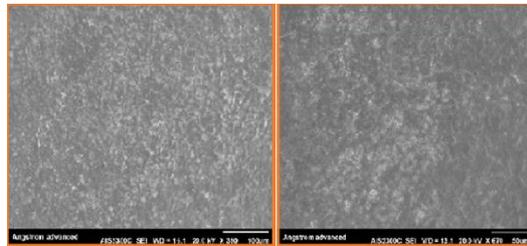


Figure 11: SEM of coated cpTi by different magnifications (100µm, 50 µm)

B. PHASE IDENTIFICATION

Phase analysis was detected by X- ray Diffractometer, using Cu K α radiation. The 2θ Angles were swept from 20- 60° in step of one degree. The X-ray diffraction pattern for the nano-Titania coated samples is showed in (figure 12).

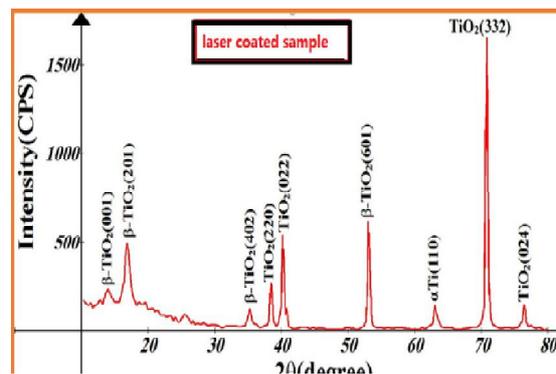


Figure 12: X-ray diffraction pattern of cpTi sample coated with TiO₂ by using laser deposition technique.

C. MICROHARDNESS TEST

For microhardness test, an average of three readings of three cpTi samples from each group, uncoated samples and nano- Titania coated samples by laser technique, were taken by using the Vickers microhardness tester. The Vickers hardness was measured using a (1) kg load and a (5) sec loading time to determine the indentation hardness. The average Hardness Vickers (HV) numbers are 232.6 and 256.7 for uncoated samples and nano-Titania coated, respectively.

D. ELEMENTAL COMPOSITION:

Energy Dispersive X-ray spectroscopy (SEM/EDX) analysis was used to determine the main components of uncoated and nano- Titania coated samples surfaces, including weight and atomic percentages of the main elements, (table 1, 2).

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Table 1: EDX analysis for uncoated samples:

Element	Weight%	Atomic%
C K	8.93	23.37
O K	13.03	25.59
Ti K	77.21	50.65
Zn K	0.83	0.40
Totals	100.00	

Table 2: EDX analysis for coated samples:

Element	Weight%	Atomic%
C K	6.62	14.95
O K	28.62	48.55
Ti K	63.50	35.98
Zn K	1.26	0.52
Totals	100.00	

IV. DISCUSSION

A. MICRO AND NANO-MORPHOLOGICAL ANALYSIS

The optical microscopic images for the coated samples, (figure 6), showed uniformly distributed and highly homogenous coating without any formation of cracks and irregularity in distribution. In nanoscale and by using SEM examination, (figure 11), the coating film showed somewhat rough morphology with thin continuous film and well distributed coating particles on the substrate surface without the presence of any loss parts, irregularities and cracks on coating film. The absence of defects in the coating films may be due their low thickness and/or the sintering conditions in which the high temperature generated by short duration laser repeated high energy pulses were associated with the cooling effect of the suspension, where the samples were immersed during coating procedure.

B. FILM THICKNESS

From the thickness measurements, the results demonstrate that the modified laser technique produced a thin Titania film coating, which was not exceeding 2µm. However, an increase in film thickness can occur due to high treatment temperature in the absence of cooling effect⁽¹⁰⁾. Therefore, thin film thickness produced by this technique might be produced due to the cooling effect that was associated with the high treatment temperature formed by high energy laser pulses.

C. SURFACE ROUGHNESS

The results of (AFM) surface roughness of Titania deposited films, (figure 7), revealed that nodules and peaks were of an average roughness of (3.44) nm and of surface area ratio of (7.56) nm. Therefore, this modified laser deposition technique can be considered as an effective method in changing the surface features of titanium substrate surface into nanoscale features. Consequently, if this technique is used to coat the titanium dental implants, these nano scale surface features can markedly improve the implant surface behavior; this agrees with **Refaat and Hamad**⁽¹¹⁾ who revealed that the increases in the roughness of the titanium surface can lead to increase the surface area of the implant and therefore promoting the opposition of bone.

D. XRD PHASE ANALYSIS

It is clear from of the XRD pattern, (figure 12), that the surface of the samples were well covered with titanium oxide layer, because most of the diffraction peaks could be indexed to titanium dioxide, corresponding to Joint Committee on Powder Diffraction Standards (JCPDS) of the International Centre for Diffraction Data (ICDD, file # 44-1294 for Ti, # 11-0218 for TiO₂). Also there was broadening in the recorded XRD peaks which means that the coatings have small crystallite size. This is in agreement with **Ladd and Palmer**⁽¹²⁾ who mentioned that the decrease in the crystallite size causes broadening of the recorded XRD peaks.

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E. MICROHARDNESS EVALUATION

Vickers microhardness tests for the uncoated and coated samples indicate that average (HV) numbers for the coated sample was higher (256.7 HV) than that of the average (232.8 HV) of uncoated ones. The increase in microhardness value after using of modified laser deposition technique might be due to the formation of high quality Titania film which are strongly bonded to the titanium surface.

F. MATERIAL CHARACTERIZATION:

The microstructural Energy-Dispersive X-ray spectroscopy (EDX) analysis, (table 1, 2), of uncoated and the coated samples showed that the main elements of the surfaces were Ti and O. However, the coated samples showed a markedly increase in the oxide percentages as compared with uncoated one. This increase in oxygen percentages were occurred as a result of the presence of the Titania coatings that increase the surface titanium oxide thickness of the titanium substrates.

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