SURFACE TOPOGRAPHY AND CHEMICAL ANALYSIS OF SURFACE TREATED TITANIUM ALLOY

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ABSTRACT

Statement of problem: The use of titanium has increased for metal ceramic crown and bridge restorations, as well as for use in titanium implants. Some surface treatments of titanium have been introduced to enhance the titanium bond strength; however, a more reliable, easily used dental laboratory method has not been established.

Objectives: The purpose of this in vitro study was to investigate the effect of Sandblasting -particle abrasion, Plasma focus and anodization as a titanium (Ti-6Al-4V) surface treatment on the surface topography variations, surface morphology and chemical composition.

Material and methods. A total of 75 uniform discs of titanium alloy (Titanium International (Medically pure alloy). (Ti-6Al - 4V)ELI, Carpenter.) were supplied as discs with 4mm diameter, 4mm thickness and 12.5 mm² surface area. Discs were divided into 4 groups (n=15) to receive different surface treatments: Group I: control group (TC), no treatment was performed. Group II: Sandblasting group (TS) was divided into two subgroups (TS1 and TS2) according to the particle size of Al₂O₃ powder. The titanium discs were grit-blasted using (50 and 250μm) grit-size of Al₂O₃ particles. Group III: (Plasma focus group TP). Group IV: (Anodizing group TA). surface topography characterization was done to investigate the effect of surface treatment on the surface roughness, surface morphology and surface composition using: interference profilometer microscope (IPM), X-Ray Diffraction (XRD), Environmental Scanning Electron Microscope (EDAX). ANOVA test was used to compare between means of the different groups. Tukey's test was used for pair-wise comparisons between the groups when ANOVA test is significant. The significance level was set at P ≤ 0.05. Statistical analysis was performed with SPSS 16.0® (Statistical Package for Scientific Studies) for Windows.

Results. Statistical analysis (ANOVA) showed that The Ra value was found to be higher (~0.32 - 0.85 nm) for treated samples as expected when compared to the untreated sample (0.04 nm). Scanning electron microscopic (SEM) analyses of both untreated and treated titanium alloy surfaces of the discs displayed differences in the surfaces topography of treated titanium alloy discs when compared with the untreated discs. At EDAX analysis, the elemental analysis shows that there are fundamental differences between them. XRD patterns of titanium alloy discs before and after different types of surface treatment. The discs displayed differences in the surfaces composition of treated titanium alloy discs when compared with the untreated discs.

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INTRODUCTION

The use of commercially pure titanium (CP Ti) and its alloys in implants and prostheses has increased due to their excellent biocompatibility, high strength to weight ratio, corrosion-resistance and low cost. High relative durability and creep-resistance. Light in weight, no cytotoxic and allergic problems. Potential biological hazards and difficult handling are their main disadvantages.\[1-3\]

The need for new metal-based components for a good quality of life increases. So, Surface characterization has been widely used to design material properties with specific purposes, including biomedical applications. Titanium and its alloys have been successfully used for manufacturing metallic implants and dental prostheses.\[4\] The literature lacks about the solutions to enhance bond strength values between cement and the metal substrate. Hence the development of surface modification is a very important.

However, many difficulties remain to be solved before titanium can be routinely used in prosthodontic applications. The usual problem encountered clinically is the need for a durable chemical connection between metals, ceramics and veneers, or luting cements.\[5\] Surface treatments are common methods for improving the general adhesion properties of a material, by facilitating chemical and micromechanical retention between different constituents.\[6\]

In general, surface treatment when applied to metallic alloys can be thought to consist in affecting three distinct stages of physico-chemical modifications. The first stage is surface cleaning: the removal from the surface of oils and other organic lubricants used during the samples’ manufacturing and cutting process. Secondly, the superficial native oxidation layer has to be removed by etching. Finally, surface chemical conversion could be sought, giving the final state of the surface.

In an attempt to improve the quantity and quality of the titanium alloy interface, surface treatments such as surface machining, acid etching, electropolishing, anodic oxidation, sandblasting or plasma-spraying may be undertaken to induce chemical modifications associated with alterations of the surface topography. It has been shown that methods of alloy surface preparation can significantly affect the resultant properties of the surface and subsequently the biologic responses and rates of adhesion that occur at the surface. Recent studies have shown that the success or failure of dental restorations can be related not only to the chemical properties of the alloy surface, but also to its micromorphology. So the interfaces can be affected by surface topography on a macroscopic as well as on a microscopic level.\[6-13\]

According to the clinical needs, different surface modifications have been proposed. These methods are: mechanical, chemical and physical methods according to mechanism of the modified layer on the surface.\[1\] Thus, the aim of the present study was to study the effect of different methods of treatment of titanium surfaces on the surface topography and chemical composition. Surface analysis of titanium was Performed.
MATERIALS AND METHODS

75 uniform discs of titanium alloy (Ti–6Al-4V) (Titanium International (Medically pure alloy). ELI, Carpenter.) were supplied as discs with 4mm diameter, 4mm thickness and 12.5 mm² surface area. Each titanium alloy disc was placed separately in clean glass flask containing distilled water to be washed for 30 minutes in an ultrasonic bath, to be sure the complete cleaning of the discs. All discs were dried at room temperature with air using air dryer. The prepared discs were divided randomly into 4 main groups according to the method of the surface treatment applied: Group I: control group (TC), no treatment was performed. Group II: Sandblasting group (TS) was divided into two subgroups (TS1 and TS2) according to the particle size of Al₂O₃ powder. The titanium discs were grit-blasted using (50 and 250μm) grit-size of Al₂O₃ particles. Group III: Plasma focus group (TP). The samples were treated using nitrogen gas. Group IV: (Anodizing group TA). For Group II: A special Copper holder was designed and constructed to fix the distance between the disc and the nozzle of the blasting machine. The first subgroup (TS1) was sandblasted using a 50μm aluminium oxide particles size, while the second subgroup (TS2) was sandblasted using a 250μm aluminium oxide particles size. All discs were sandblasted at room temperature by high purity (Al₂O₃), in sandblasting machine (Dental form – Torino Italy). Under standard conditions of pressure, time, and distance, using continuous constant motion of the blasting pressure (3 bar), time for (10 seconds), and at a fixed distance (10cm). The blasted discs were placed separately in glass flasks containing distilled water to be washed for 10 minutes in an ultrasonic bath, and then dried with air at room temperature, and became ready for cementation. Group III: Plasma focus group (TP). The 15 discs of titanium alloy (TP) were introduced into the DPF chamber (UNU/ICTP, PPF plasma focus device of Mather type) and mounted axially above the anode with the help of specially fabricated wooden holder to adjust the distance between the rim of the anode and the disc (2.5cm). Group IV: Anodizing group (TA): The 15 discs of titanium alloy were use. Special holder was designed and constructed to housing the titanium alloy disc during immersion in acidic solution. Just prior to anodization, each titanium sample (TA) was soaked in a specific acid solution mixture (150ml Hydrogen peroxide, 80ml nitric acid and 60 ml hydrofluoric acid) for 3 minutes, Titanium was then removed and rinsed with deionized water then was cleaned ultrasonically for 5 minutes. Next, the sample was used as an anode in an electrochemical cell, parallel to a platinum mesh acting as the cathode; the 1M phosphoric acid and 1%hydrofluoric acid solution served as an electrolyte solution with PH = 5. Then completed the circuit. A constant voltage of 20 V* (Power supply DC, MUNK, PSP Vari plus, 25V/50 A) was then applied to the circuit for 30 minutes, with 100RPM stirring (Wise Stir feedback, DAIHAN Scientific, MSH-10, Ger). After the anodization process, the submerged samples were then placed in a solicitor for 10 minutes, rinsed and then soaked in deionized water for 2 minutes, and then dried in air at room temperature, and became ready for cementation.

Surface topography characterizations

After surface treatment, surface topography characterization was done to investigate the effect of surface treatment on the surface roughness, surface morphology and surface composition using:
1- Interference profilometer microscope (IPM)
2- X-Ray Diffraction (XRD)
3- Environmental Scanning Electron Microscope EDAX

1- Interference profilometer microscope (IPM)

The surface microtopography of the treated titanium discs was characterized by evaluation of the surface roughness using ZYGO Maxim-GP 200
profilometer which is a general purpose surface optical profiler that measures the microstructure and topography of surfaces in three dimensions. Computerized phase stepping interferometer (PSI) upgraded with scanning white light interferometer (SWLI) and advanced surface texture software which analyzes areas as well as profiles and step height. average surface roughness (Ra) of each disc after each surface treatment was measured. The measurement was carried out by interference microscope with a measurement length of 5mm. For each specimen disk, 3 measurements were recorded and averaged. The (Ra) values were obtained from 15 specimen disks and data were averaged, indicating a total of measurements for each disk. Images were recorded in air and room temperature. Data were analyzed and the following selected 3D roughness parameters were calculated: the arithmetic average of the absolute values of surface height deviations recorded within the sampling area (Ra) in nm, density of summits which describes number of local maximum per area (Sds), and surfaces area ratio which expresses the ratio or the percentage between the surface area (taking the z height into account) and the area of the flat x–y plane (Sdr).

2- X-Ray Diffraction (XRD):

XRD was performed in order to demonstrate the constituent phases of surface and changes of the different dental alloys systems. Using an X-Ray Diffract meter (X, PERT PRO Diffractometer Philips .Ain –Shams University.) with a copper target (Cu k α = 1.54060) and Nickel filter, selected samples of each group were recorded. Data of XRD were based on Bragg’s equation: $n \lambda = 2d \sin \theta$

Where; $n =$ Integral number. $\lambda =$ Wave length. $d =$ Interplanar space. $\theta =$ Diffraction angle

3- Environmental Scanning Electron Microscope

One representative sample was chosen from each group to be scanned using Environmental Scanning Electron Microscope (ESEM Environmental Scanning Electron Microscope QUANTA 200, FEI, Nationality collected of Netherlands (Multinational) in Antiquities Research Center, Cairo, for surface examination. Scanning Electron Microscope with the Energy Dispersive X-ray (EDXA) attachment was used to investigate surface morphology and the elemental composition of titanium alloy disc before and after surface treatment.

RESULTS

Statistically, data were presented as means and standard deviation (SD) values. ANOVA test was used to compare between means of the different groups. Tukey’s test was used in the procedure of pair-wise comparisons between the groups when ANOVA test is significant. Pearson’s correlation coefficient was used to determine significant correlations between the different variables. The significance level was set at $P \leq 0.05$. Statistical analysis was performed with SPSS 16.0® (Statistical Package for Scientific Studies) for Windows.

I) Results of surface topography characterizations

Topography of modified surfaces is extremely important as it directly affects surface roughness and eventually, the adhesion and bond strength on the surface.

I- Interference Microscope.

1. a- 3D IPM topographies:

The constructed 3D IPM topographies of the surfaces of the different titanium alloy groups were shown in Figure (1) the length and the width of the scanning areas were presented in the x and y axes respectively in μm while the amplitude of surface characteristics were presented in the z-axis in μm. The relative height of surface characteristics were color-coded and were ranged from dark blue for deepest area to red for the highest areas. all the different titanium alloy groups were characterized by rough surface that observed all over the treated surfaces as an area of elevations and depressions with different dimension scales.
1. b- Surface roughness (Ra) analysis:

The roughness values (Ra, Rq and Rrms) calculated from the IPM images. The mean and standard deviations of the roughness parameters for each group were tabulated in Table (1) and Figure (2). Where Ra is the Average height of the analysed area (nm), Rq is the Root-mean-square of the surface topography (nm) and Rrms is the Skewness of topography height distribution of analysed area.

The Ra value was found to be higher (~0.32 - 0.85 nm) for treated samples as expected when compared to the untreated sample (0.04 nm). Control group TC showed the statistically significantly lowest mean Ra, Sandblasting (50 µm) TS1 showed the statistically significantly highest mean Ra. This was followed by Plasma Focus group TP then Sandblasting (250 µm) TS2 which showed lower values. Anodizing groups which showed much lower mean Ra values.

II) Morphological and elemental analysis of the surface

The results of Energy Dispersive X-ray Chemical Analysis (EDAX) and scanning electron micrographs of the surface of titanium alloy samples before and after surface treatment showed initial characterization of the Titanium alloy surfaces.

TABLE (1): Means, standard deviation (SD) values and results of ANOVA test for comparison between Ra (measured by interference method) in the all groups
1- Energy Dispersive X-ray Chemical Analysis (EDAX)

1. a-Results of scanning electron microscope (SEM):

Scanning electron microscopic (SEM) analyses of both untreated and treated titanium alloy surfaces of the discs displayed differences in the surfaces topography of treated titanium alloy discs when compared with the untreated discs (Figure 3). The untreated discs showed a well-defined unidirectional pattern due to machining preparation, so the surfaces revealed no distinctive topographic features.

SEM photos revealed distinct patterns of surface topography of all kinds of surface-modified titanium alloy discs. The surface treated disc revealed pores and grooves formation. Pores were observed as the most important descriptive pattern for the treated surface. Different pore sizes and distribution were observed. The surfaces showed a great increase in roughness and micro textured property (significant waviness and numerous irregular micropits and indentations). However, these characteristics result in significantly different values of the means when compared with the discs that did not receive this surface treatment.

By examining the SE photomicrograph of TS group using either 50 μm or 250 μm blasting surfaces are characterized by complete disappearance of the machining grooves, high peaks, deep valise and well defined irregularities with more uniform size of surface roughness. Observable differences were noted between alloys blasted by 50 μm or 250 μm grit size particles. A number of Al2O3 blasting particles were embedded in the surface.

Examining the SE photomicrograph of TP group reveals a high density of lamellar-shaped crystals on the surface. These crystals improve the adhesive properties of the surface by increasing the surface area available for bonding. Also, the adhesive can flow in and out of the irregularities on the surface thus providing good mechanical interlocking. The photomicrographs are given in the following order: in the center of spot and in the periphery of the spot. These micrographs show that the treated surface is not homogenous, and has a localized effect spot shape.

Examining the SE photomicrograph of titanium alloy disc group treated by anodization, surface was characterized by small and regular round porosity and larger scale surface roughness. Figure is a micrograph of TA treated surface. It shows a high degree of surface roughness compared to the non treated surface. The surface resembles a honeycomb with a high pore ratio, which the adhesive enters to provide good mechanical interlocking resulting in high adhesive bond strength.

1. b- Results of EDAX:

The results of Energy Dispersive X-ray Chemical Analysis (EDAX) of the surface of titanium alloy samples before and after surface treatment are

![Figure 3: a- SE photomicrograph of TC gr., b- TS1 gr., c- TS2 gr., d- TP gr., and e- TA group at 1000x]
shown in Figures (4). Elemental analysis within the indicated region of TC group shows the chemical composition of the untreated surface (TC). The presence of main and large peaks correspond to peaks of titanium, aluminium, vanadium, and it is therefore considered to be a compound of Ti-Al-V. Some contaminant such as N was present on the surface as an impurity.

A direct comparison of the survey spectra for an unmodified surface and modified surfaces illustrated changes. These changes were reflected in terms of elemental composition for various surfaces created by surface treatment. The elemental analysis shows that there are fundamental differences between them. At EDAX analysis, type of elements within TS group, was clarified. Oxygen peak in addition to peaks of titanium, aluminium and vanadium suggested that there is more oxygen on the treated surface compared to that of a TC surface. Thus, during the treatment process the alloy surface was oxidized and a fresh oxide layer was formed on the surface. It was noticed an increase in aluminium concentration as well as oxygen content also; there was a decrease in titanium and vanadium concentration. Nitrogen with lower concentration was observed on the surface as an impurity. Grit blasting with alumina not only affected the micromechanical roughening of the surface, but it left alumina particles embedded in the surface. Part of titanium loss may be leached out during sandblasting and other part may be combined with oxygen in the form of oxides taking into account the build up of oxygen in the sample. However the EDAX technique does not differentiate between elemental and combined titanium.

A comparison of the survey spectra for TC surfaces and TP surfaces illustrated changes in titanium, aluminium, and vanadium and nitrogen composition of the top surface layer before and after treatment. It can be noticed that no peak corresponding to any impurity element, other than those supposed to be present in TiN film. There was an increase in Nitrogen. It is important, as in focus device, that the TiN thin films are deposited at relatively higher pressure of 2.5 mbar of nitrogen. We noticed an increase in oxygen composition. There was a decrease in titanium, aluminium and vanadium contents. Carbon was again present on the surface as an impurity.

A comparison of the survey spectra for TC surfaces and TA surfaces illustrated changes in titanium, aluminium, and vanadium and nitrogen composition of the top surface layer before and after treatment. It can be noticed that no peak corresponding to any impurity element. We noticed an increase in oxygen composition. There was a decrease in titanium, aluminium and vanadium contents. Carbon was again present on the surface as an impurity. We noticed an increase in oxygen content with increase in oxygen peak in addition to the peak of silica. This suggests that there is more oxygen on the treated surface compared to that of a TC surface. Thus, during the treatment process, the alloy surface was oxidized and a fresh oxide layer was formed on the surface.

![Fig. (4): EDAX spectra](image)

**III - Chemical analysis of the surface**

Figure (5) showed XRD patterns of titanium alloy discs before and after different types of surface treatment. Control group shows Ti peaks at $2\Theta = 35^\circ, 38^\circ, 40^\circ, 52^\circ, 70^\circ$, and $76^\circ$. Peaks at $2\Theta = 41^\circ$ and $63^\circ$ are due to AlTi$_3$. Peaks at
We also noticed a low ratio between the two peaks (37.5-40°). Sandblasting group shows no extra peak at 2Θ =35° because of the absence of chemical changes. The first peak around 2Θ = 37° is split presumably because of selective erosion of alloys constituents. The peak around 77.3° is decreasing in intensity due to erosion of corresponding phase. Plasma focusing group shows new two peaks in the form of wings at 37° and 43.2°, which was assigned to titanium nitride (Ti2N). Peaks due to original alloy vanish to broad bands due to transmation of the alloy components to non- crystalline product following intensive heating. Anodizing group shows prefential etching and anodization of titanium alloy giving new peaks of TiO at 35.37° and 63.39°. The relative increase of the peak at 77.698 assigned to (AL-V) binary system is due to relative enrichment in AL and V following depletion of titanium. The decrease in original peaks at 38.7° is mainly due to depletion of Ti-Al-V system. The increase of the peak at 40.398 (3.65→5.97) is due to build up of TiO that has a strong emission at this value. The presence of H2O2 as well as anodization process plays a role in oxidizing the more labile titanium constituents.

DISCUSSION

The selection of alloys for the fabrication of prosthodontic restorations depends on the physical and chemical properties desired. Allergic reactions may be a problem due to the presence of nickel in base metals. In a study comparing conventional Co-Cr alloy and Titanium in terms of biocompatibility, sensitivity or allergic reactions were found to decrease with the use of Titanium.

Titanium may be considered as being a relatively new engineering material. It was discovered much later than the other commonly used metals, its commercial application starting in the late 1940s, mainly as structural material. The use of titanium alloys as biomaterials has been growing due to their reduced elastic modulus, superior biocompatibility, high strength to weight ratio and enhanced corrosion resistance when compared to more conventional stainless steel and Co-Cr alloys. Ti-6Al-4V, the most common titanium alloy is still the most extensively used titanium alloy for medical applications. Some of the most important techniques for improving the properties of Ti alloy surfaces are: Mechanical methods for surface treatment can be divided into methods involving removal of surface material by cutting (machining of the surface), abrasive action (grinding and polishing) and those where the treated material surface is deformed by particle blasting. Chemical methods are based mainly on chemical reactions occurring at the interface between titanium and a solution (solvent cleaning, wet chemical etching, passivation treatments and other chemical surface treatments such as hydrogen peroxide treatment). Electrochemical surface methods are based on different chemical reactions occurring at an electrically energized surface (electrode) placed.
in an electrolyte (electropolishing and anodic oxidation or anodising).\textsuperscript{[14]}

During the present research work, we used four groups (sandblasting group, Plasma group and anodizing group in addition to control group) to create a new titanium surface combining all the aforementioned surface texture features. In this study titanium alloy without surface treatment was taken as a control group. The present study showed that precise method selection and the sequence of processing played the main role in preparation of the rough titanium surface. The knowledge of the surface characteristics of different alloys after surface treatment is important to improve the bond strength to the alloys.

Surface characterization and Surface morphology was evaluated using scanning electron microscope (SEM). The associated energy-dispersive spectrometer (EDAX) provided qualitative information about surface elemental composition. X-Ray Diffraction (XRD) was used to characterize the external layer of each group in order to demonstrate the constituent phases of surface and changes of the different dental alloys systems. The topography of samples with a scanning area for each group was quantified through three-dimensional (3D) metrology using IPM. Scanning of the treated titanium discs was performed (Three dimensional) parameters are related to all surfaces. 3D indices are presented in this study because all chemical and biological processes occur throughout the surface, and, hence, 3D parameters are more representative.

The topographical parameters evaluated the roughness values (Ra, Rq and Rrms) calculated from the 3D IPM images, where Ra is the average height of the analyzed area (μm), Rq is the Root-mean-square of the surface topography (μm) and Rrms is the Skewness of topography height distribution of analyzed area. The Ra and Rq parameters are strongly correlated, which gives plots with the same appearance. Since the Ra parameter is more widely used in the dental literature. The Ra value was found to be higher (~0.32 - 0.85 nm) for treated samples as expected when compared to the untreated sample (0.04 nm). Wang and Fung\textsuperscript{[15]} have indicated that the unmodified titanium surface produces a weak, porous, non-protective and non-adherent oxide layer that is unsuitable for bonding.

The sandblasting procedure roughened the surface of the titanium alloy, creating a mechanical interlocking with the resin cement. The increased roughness can also form a larger surface area for bonding. IPM, EDAX and SEM observation partially confirmed this mechanism: the surface of sandblasted titanium alloy showed a roughness pattern with shallow pits; forming “micoretention-space”, generating micromechanical retention at the bonding interface. Van Dalen et al\textsuperscript{[16]} reported that after sandblasting, many Al2O3 particles were attached to the metal surface, which could affect the bonding performance. This finding concurs with those of Reyes et al.\textsuperscript{[17]} Airborne-particle abrasion likely improves the bond strength by removing loosely attached furrows, overlaps, and flakes of metal created by grinding procedures, provides mechanical interlocking, increases surface area, and increases wettability.

It was found that sandblasting is frequently used in adhesive dentistry, especially for pretreating acid-resistant materials. It can roughen the surface of a restoration, making it honeycomb like, which is expected for micoretention.\textsuperscript{[18]}

Sandblasting creates surface roughness and increases the mechanical and chemical bond strength between metal and acrylic resin. Mechanically removes not only the debris, but also the metal oxide layer and other substances. However, because of the reactivity of titanium, even when the oxide layer was removed from the surface, re-oxidation of the titanium proceeded immediately. After sandblasting, the titanium surface was covered with a thin, stable oxide film. In view of this, we postulate that the thin oxide film produced on the titanium is essential for strong bonding The choice
of a chemical bonding system for prosthodontic applications may depend on factors such as expense, availability, time requirements, and the shelf life of the perishable components.[19,20]

In this study by utilization of IPM microscope after different surface treatment, it was found that sandblasting (50 μm) showed the statistically significantly highest mean Ra. This was followed by plasma focus group then sandblasting (250 μm) which showed lower values and control group showed the statistically significantly lowest mean Ra. Also it was found that sandblasting (50 μm) showed the statistically significantly highest mean % change in surface area and control group showed the statistically significantly lowest mean % change in surface area.

In current study By utilization of an XRD microscope after the sandblasting and ultrasound cleaning, observed the presence of peaks at 40.94° and 40.295° are attributed to titanium oxides, (Ti₆O and Ti₃O) respectively. Also peak at 22° and 24° are attributed Lenoblite (v2+4O4.2H2O).

In this study by utilization of an EDAX microscope after the sandblasting and ultrasound cleaning, we observed the presence of 13.41wt% of alumina, an important compound affecting the bond to the resin cement. This is supported by the findings of Kern and Thompson (1994b) [21], the alumina particles are firmly attached to the titanium surface. Other sandblasting influence is in the phenomenon of alumina particles incrustation during the sandblasting procedure. These particles stay stuck on the titanium surface because of the velocity and the pressure that they hit with and cannot be removed even by ultrasonic cleaning or acid etching. So, these non-removable alumina particles become responsible for the chemical bond of the Alloy Primer and silane agents to themselves, increasing the bond strength of cement.[22, 23, 24]

The roughness values are increased with increasing grade of blasting. It has been found that the intermediate particle sizes can influence a homogeneous distribution. The surface defects are found in the largest particles. A correlation between roughness amplitude and particle size is still detectable but not dramatically appreciable. The surface roughness values depend on particle size rather than surface composition.[25, 26] However, the alumina sandblasting induces a considerable amount of titanium surface contamination. Thus, the treated surfaces are not pure titanium but rather a composite structure of pure titanium, titanium oxides and aluminum oxides.[27]

Even though Lim et al (2003) [28] have indicated problems such as contamination and distortion of the prostheses after sandblasting, Kern and Thompson (1994) [21] evaluated the volume of titanium lost after sandblasting and concluded that abrasion was not critical for adaptation of the restorations. Also it was found that the coarser particle size of alumina improves the bond strength of polymer-glass composite to cast titanium. However, sandblasting restorations, especially with the 250 μm alumina (Al₂O₃), has the potential to remove significant amounts of substances and could affect the clinical adaptation of the prostheses. Material loss that results from sandblasting and sandblasted rough surfaces is important to the clinical fit of restorations.[29]

Tiller et al (1985) [30] and Segerström and Ruyter (2009) [31] reported that when blasting particles hit the metal surface, their kinetic energy is transformed to thermal energy and the temperature exceeds the melting point of the alloy. Silica particles will be anchored in the metal surface and form a thin porous layer on the metal surface: this coating on its own does not provide a sufficiently reliable bonding to the metallic structure.

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surface roughness values depend on particle size rather than surface composition.[25, 26] Plasma treatments and particle beam irradiation (electrons, photons, neutrons and ions) are well established to not only induce growth of the crystallinity degree, but also to create more bioactive surfaces, improve the adhesion with metallic films, increase the wettability, improve the mechanical properties, produces more favorable surface for graft copolymerization, increase the electrical conductivity, improve cell adhesion control for biomedical applications, etc.[32, 33] The micrographs of plasma focus treated surfaces obtained by scanning electron microscopy reveal that Plasma focus treatment leaves the surface resembles high density of a lamellar shaped crystals with a high pore ratio. These lamellae improve the adhesive properties of the surface by increasing the surface area available for bonding. It shows a high degree of surface roughness compared to the HCl treated surface. From IPM, it was found that mean of Ra value of TP (0.73). Also, the adhesive can flow in and out of the irregularities on the surface thus providing good mechanical interlocking.

Rawat et al (2003)[34] found that he highly energetic nitrogen ions from the following focus shot, besides helping in formation of titanium nitride, can also cause the etching of the film deposited in the previous shot. The etching of the deposited film is dependent on the energy and flux of the ions that are impinging the film surface. It is a very common experience that focusing action becomes stronger as focus gets stabilized after firing a few focus shots resulting in generation of higher energy, higher flux ions causing greater radiation damage and thus lower deposition rate.

The rapid temperature rise during ions bombardment by each successive shot may assist the migration of defects within the film and thus improves its crystallinity as well. Moreover, the filling gas species ions are formed and accelerated earlier than the ablated titanium ions. These energetic filling gas species ions reach the substrate first causing etching and hence cleaning of the substrate surface prior to deposition.[35]

It could be thus assumed that the dense plasma focus of Ti6Al4V alloy samples appears to partially produce all three stages of surface treatment: surface cleaning from organic contaminants, Al (OH)$_3$ fragile oxide removal and finally surface functionalization denoted. Though it is difficult to distinguish the predominant effect of the plasma and estimate its efficiency on each of the aforementioned stages, attention should be drawn to the organic contamination removal, which has a practical interest. However, it is not possible to know whether this cleaning is total or partial. The remaining carbon (0.841 wt%) on the surface can be either due to remaining lubricants and/or to the natural contamination after the short exposure to ambient conditions, prior to the EDAX analysis of the samples.

Significant progress has been made recently in the application of anodizing as a method of forming nano-structural layers of oxides on metal surfaces. Formation of high level of the organization of pores on large surfaces as well as controlling the size and arrangement of pores. Formation of oxide layers conducted in the phosphoric acid solutions with additions of fluoride ions. Anodic films on titanium have been of great interest due to their industrial applications. Anodizing can also result in the adsorption and incorporation of biologically important species into the oxide layer. Such surface layers are of a great importance for medical implants, which should not only be corrosion resistant in a biological environment, but also compatible with tissue response. Formation of such layers in phosphate solutions is of great importance due to the possibility of their incorporation into the layer and influence the bioactivity. [36]

A micrograph of anodizing treated surface shows a high degree of surface roughness compared to the non treated surface. The surface resembles a
honeycomb with a high pore ratio, which the adhesive enters to provide good mechanical interlocking. From IPM, it was found that mean of Ra value of TA (0.51). Also, the adhesive can flow in and out of the irregularities on the surface thus providing good mechanical interlocking. The EDAX analysis revealed that the highest amount of oxides in surface layer is obtained when using 1M H₃PO₄+H₂O₂. Due to the presence of phosphates in the anodic layer formed on titanium materials in the phosphoric acid solutions the obtained surface layers were highly bioactive in comparison to ordinary oxides. In this study, the HF concentrations in the electrolyte used for the cathodic reduction process were selected in order to achieve a weak, a moderate, and a strong etching effect on the titanium surfaces, without introducing surface cracks.[37]

CONCLUSIONS

Based on the previous results the following conclusions could be obtained: Initially, the surface treated titanium alloy demonstrated significantly high roughness than the nontreated titanium alloys. And it was recognized that the change in alloying elements content and % have different influences on the surface of titanium alloy. Finally, the surface composition was altered probably because of reactions with the used material.

REFERENCES