Roughness and mechanical properties of electron-beam surface modified and TiN/TiO$_2$-coated Ti6Al4V alloy

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Abstract. In this study, we used PVD deposition of TiN/TiO$_2$ coatings on polished and electron-beam-treated Ti6Al4V alloy to explore the changes in the surface roughness and mechanical properties of the coated systems. After the electron-beam treatment (EBT), the average surface hardness and roughness ($R_a$) increased from 323±5.62 HV$_{0.2}$ and 0.14±0.004 μm up to 387.5±9.33 HV$_{0.2}$ and 1.58±0.05 μm, respectively. After coating with 3.7-μm thick TiN/TiO$_2$, the average $S_a$ roughness and nanohardness of the film on the polished substrate reached 0.87±0.1 μm and 13.05±2.07 GPa while that on the EBT was equal to 1.57±0.2 μm and 9.02±2.15 GPa, respectively. However, the comparison of the coefficient of friction (COF) evolution of the substrates and the coated specimens indicated a COF decrease by about 0.18±0.03 for the coated EBT alloy as compared with the polished and EBT substrates, whose average COF were 0.45±0.04 and 0.38±0.06, respectively. A high average COF (0.68±0.16) was registered for the coated as-received alloy because of the gradual and complete wearing off of the film during the test. These results indicate that the combination of initial EBT of the Ti6Al4V alloy with PVD deposition of a TiN/TiO$_2$ coating could substantially improve the roughness and tribological properties of the coated systems.

1. Introduction
Experiments with animals have shown that the body accepts better the rough surface of implants because of the improved tissue adherence to roughened grafts [1]. A rough surface can be produced by machining, chemical, electrochemical, electrical discharge processes, or by irradiation with high-energy fluxes (e.g., electron or laser beams). Among these, the electron-beam treatment is characterized by beain a non-oxidizing process with precisely controlled energy input and process parameters that benefit the improvement of the surface structure, roughness, and other properties. The process of irradiation triggers fast heating and cooling that induce structural transformations, melting of the surface and changes in the surface roughness.

The most widely recommended titanium alloy for orthodontic and orthopedic implants today is Ti6Al4V. However, it suffers from a lack of quick and effective osseointegration and degradation due to corrosion in the aggressive body environment that releases harmful V and Al ions [2]. This issue can be addressed by applying superficial treatment, such as wet or spray processes, chemical treatments, or deposition of coatings for osseointegration. The PVD-deposited TiN/TiO$_2$ film appears to be such a bioactive coating that has been proved to enhance the corrosion resistance and improve cells viability, adhesion, and bone mineralization [3, 4]. However, biocompatible coatings can only be considered safe if possessing suitable mechanical properties that can make them functional. Inappropriate hardness and elastic modulus and a high coefficient of friction could lead to a low bio-fixation of the material and failure of the implant in service. Lower Young’s modulus values of hard coatings close to
that of the cortical bone (17 GPa [5]) can be considered beneficial since a large elastic modulus mismatch between implant and bone may cause stress shielding and bone resorption under load [6]. It is widely recognized that the substrate material plays an important role in determining the coatings’ wear resistance and mechanical properties [7]. This paper reports our studies on the effect of electron-beam treatment of Ti6Al4V substrates on the mechanical response of TiN/TiO₂ coatings by using AFM, nanoindentation and ball-on-wear tests.

2. Experimental procedure

Samples with chemical composition 6.22% Al, 3.57% V, 90.38% Ti (in wt %) and dimensions of Ø22×4 mm were cut by electro-erosion from pieces of Ti6Al4V alloy. The as-received (AR) samples were ground and finely polished. Electron-beam treatment (EBT) was carried out by a Leybold Heraus (EWS 300/15–60) electron-beam installation. The following technological parameters were applied: linear scanning, electron beam current \( I = 30 \text{ mA} \), acceleration voltage \( U = 52 \text{ kV} \), speed of sample motion \( v = 2 \text{ cm/s} \), electron-beam scanning frequency \( f = 850 \text{ Hz} \). The samples surfaces were ultrasonically cleaned with absolute ethanol, acetone, isopropanol, rinsed with distilled water for 5 min, and dried. The deposition of TiN (by vacuum cathodic arc technology at 340 °C) and overlaying TiO₂ (by glow plasma discharge at 300 °C) has been described in detail elsewhere [8].

The surface morphology of the untreated and of the coated samples was assessed by scanning electron microscopy (SEM, LYRA I XMU, Tescan). Micro-Vickers hardness measurements were conducted on the top of each substrate (polished and EBT) with a load of 200 g and dwell time of 15 s using a PMT-3 microhardness (IOOMO) tester. The distance between the indents was 20 μm. The nanohardness of the coatings was investigated using a nanomechanical tester (Bruker, Billerica MA) which applied a load of 25 mN at 48 indentations with a spacing of 80 μm.

The surface topography was analyzed using a contact profilometer (Mitutoyo SJ 201 P). The samples were evaluated quantitatively for \( R_a \) (average roughness) after a tenfold scanning with a cut-off value of 0.8 mm in a direction perpendicular to the grooves caused by the local melting. The surface topology was characterized by atomic force microscopy (Q-Scope™ 250/400 Nomad™ commercial AFM system, Ambios Technology Inc). The measurements were taken by a 10-nm radius silicon tip on each coating over 80×80 μm scan areas. The coefficient of friction (COF) was determined by sliding wear study performed on a ball-on-flat tester (CSEM tribometer, normal load 2 N, linear speed 100 mm/s, time of testing 300 s) with a sliding Ø6-mm ball coated with Cr. The sliding rate and time were chosen so as to initiate wear of the coatings. The tests were conducted in air at room temperature.

3. Results and discussions

The representative SEM image of the as-received (figure 1a) Ti6Al4V alloy shows a lamellar initial structure. By using backscattered electron imaging, the \( \alpha \)-phase features were identified by their darker color since they contain aluminum atoms of lower density, whereas the lighter color of the \( \beta \)-phase features is associated with the predominant presence of vanadium atoms of higher density. The wavy surface morphology obtained after the EBT is seen in figure 1b. After the EBT, the average surface hardness and roughness \( (R_a) \) increased from 323±5.62 HV₀.₂ and 0.14±0.004 μm up to 387.5±9.33 HV₀.₂ and 1.58±0.05 μm, respectively. When observed at a higher magnification (figure 1c), it is evident that the equiaxial grains on the re-melted surface contain the martensite phase only and no parental microstructure is present. The diffusionless transformation associated with needle formation is a result of the fast cooling above \( \beta \)-transus.

A cross-section micrograph of cathodic-arc-evaporated TiN/TiO₂ coatings deposited on the surface of both as-received and EBT alloys is presented in figure 1d. The high-current density at the arc spot forms not only metal ions, electrons, and neutral atoms, but also agglomerates, or macroparticles, which are seen on the surface and the cross-section parts of the film. Because of the high bias-voltage \( (U_S = -250 \text{ V}) \) that increases the deposition flow, the concentration of drops is decreased since purification and activation occurs due to ions of evaporated material spraying the surface by [9]. After the thin transition layer of pure Ti between the coating and the substrate, the nitride layer displays a dense columnar structure with no inter-columnar voids. The thinner top TiO₂ layer displays finer
pyramidal grains seen on the surface of the droplet phases. The whole coating thickness measured in figure 1d is 3.72 μm.

Figure 1. SEM micrographs of representative areas of the a) polished AR alloy; b) EBT substrate material; c) remelted structure of the EBT alloy at higher magnification; d) cross-section of PVD deposited TiN/TiO₂ coating.

Figure 2. AFM images of the films deposited on polished (a) and EBT (b) alloy.

3D AFM images of the coatings deposited on the surface of the polished and the EBT substrates are shown in figures 2a and 2b, respectively. The average $S_a$ roughness of the film on the polished substrate reaches 0.87±0.1 μm, while that on the EBT sample is 1.57±0.2 μm. As seen in figure 2, the
The measured difference is attributed to the initial roughness of the substrates, because the PVD coatings replicate the surface topography of the substrates. The small increase in the $S_a$ values of the coated polished sample as compared with the non-coated substrate is due to the presence of macroparticles within the film (figure 2a).

![Figure 3](image3.png)  
**Figure 3.** Hardness and Young’s modulus as a function of the indentation contact depth of TiN/TiO$_2$ coatings deposited on polished (a) and EBT (b) samples.

![Figure 4](image4.png)  
**Figure 4.** Friction coefficients (a) during sliding of substrates and of TiN/TiO$_2$ coatings on polished (AR) and EBT (AR850) alloy versus sliding distance; OM images of wear track areas of the coated polished (b) and EBT (c) alloy.

The results from measuring the hardness and the elastic modulus are shown in figure 3. The average nanohardness values for the coatings deposited on the polished and EBT samples were found to be equal to 13.05±2.07GPa and 9.02±2.15 GPa, respectively, whereas those of the Young’s modulus were equal to 279.5±39.2GPa and 225.9±85.2 GPa, respectively. The drop in the hardness value of the coatings deposited on the EBT alloy could be attributed to the higher surface roughness values [10], because the flat samples exhibit better surface properties. It is seen that the standard deviation of the hardness and modulus values increase with the roughness. Bearing in mind the coating thickness, at a load of 25 mN the penetration depth is less than 10% of the film thickness and the substrate effect is negligible. The hardness decreases gradually with the increase in the indentation displacement under an identical loading force and varied indentation positions. The large contact
depths should be a result of defects in the coatings, such as voids, droplets, or other microstructure inhomogeneities under the indenter.

Figure 4 plots the evolution of the coefficients of friction (COF) of the bare and of the coated samples with the sliding time. After the initial running period, the friction coefficients of the substrates remained almost constant during the sliding tests. Because of the higher surface hardness and roughness of the EBT Ti6Al4V alloy, its average COF was lower (0.38±0.06) as opposed to that of AR and polished alloy (0.45±0.04). Regarding the coated polished sample, one can see an intermediate region of increased COF which rises to the maximum steady-state value suggesting that events occurred corresponding to the formation of deep wear debris. This fact can be attributed to the soft substrate material that is unable to withstand the friction force and, to a lesser extent, to coating delamination (figure 4b). In spite of the higher roughness of the EBT alloy, the higher substrate hardness and the characteristics of the mechanical contact resulted in a substantially lower average COF (0.18±0.03) for the EBT and the coated alloy. The micrographs of the wear tracks (figure 4c) show the delamination of some areas at the coated peaks because of the adhesive wear mechanism.

4. Conclusions
TiN/TiO2 coatings with a thickness of about 3.7 μm were fabricated using arc PVD on polished and electron-beam surface modified Ti6Al4V alloy. Nanoindentation tests showed different hardness of the coatings deposited on polished and electron-beam modified alloys at similar indentation depths, whereas the response was not dependent on the underlying substrate. Both the substrate roughness and the coating topography influenced the hardness value response measured. The COF of the coated samples was dominated by the plastic deformation of the substrate material. Since the as-received material has a lower hardness, the friction was dominated by ploughing, while that of the coated electron-beam modified Ti6Al4V indicated a more durable and protective behavior. The lower Young’s modulus values of the coating on the electron-beam modified alloy that are close to that of the cortical bone (17 GPa [11]) and its better tribological properties make the proposed surface treatment appropriate for further application in the biomedical field.

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