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Surface functionalization of titanium screws for orthopaedic implant applications

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When establishing intermaxillary fixation using bone screws, the removal of such elements represents a potential complication. In this context, the bone-screw interface plays a major role. Thus, surfaces need to be modified to interact with the human body inhibiting osseointegration but fostering bone healing. Surface coating can represent a viable way to solve this issue. Actual coating procedures and difficulties in obtaining repeatable surfaces with sufficient adhesion strength refrain industries from applying such methodology. This work presents an experimental procedure to modify screw surfaces by laser ablation and to coat them with a human-tested bioabsorbable polymer by 3D bioprinting in order to fabricate intermaxillary screws. The overall results demonstrate the effectiveness of the proposed methodology to obtain high performance titanium fixation screws.

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1. Introduction

Biomaterials interact with the biological environment exclusively through their surfaces. Thus, interfaces play a key role in dictating the success or failure of an implant. Atoms and molecules residing at the surface are responsible for its unique characteristics like organization and reactivity driving many of the biological reactions that occur in response to the biomaterial like cell adhesion, growth, blood compatibility or protein absorption. As a consequence, special methods are necessary to characterize and tailor surfaces of biomaterials. While bulk properties are well known in manufacturing of medical implants, bone-implant interface represents a critical element leading to implant success or failure. Many studies have been devoted on fabricating implants favouring osseointegration so that adverse reactions can be reduced extending the reliability and the lifetime of the implant [1]. However, critical issues arise when removable implants are considered. Surfaces of such devices need to be active enough to reduce osseointegration without inducing any adverse reaction [2, 3]. Over the decades, the evolution of osteosynthesis addressed production towards the selection of more biocompatible and performing materials such as titanium and its alloys over stainless steel, and, at the same time, conventional plating systems have been outdated by locking compression plates (LCPs) promoting fracture healing over callus formation [4]. However, the above trends brought to secondary disadvantages since, supporting direct osseointegration, may lead to bone overgrowth of the screws rising concerns about implant removal process and making it a challenging procedure [5]. Nevertheless, while there are many reports on the advantages of LCPs for fracture fixation, few studies focus on problems related to implant removal [6, 7] mainly proposing solutions related to tools helping the surgeon in the removal phase, since osseointegration takes place on screws and plate surface. Micro-strains and stresses generated at the bone-tissue interface play a crucial role in the overall biomaterial applicability and it is controlled trough micro/nano surface topography [8]. Thus, coating materials have been introduced to fulfil the above requirements. The surface properties of the coating differ significantly from the bulk material thus, compatible interfacing between the implant and the coating is a crucial factor. Several techniques are employed for coating e.g., plating, dip coating, spray deposition, etc. However, these coatings exhibit inferior mechanical strength and insufficient adhesion on the implant surface when considering critical parts such as screws or pins. Furthermore, coating instability coupled with its inhomogeneous distribution on the implant surface with complex shapes, strongly limits their clinical application [9]. Also, even though the removal surgery is supposed to be dependent solely on the purpose of the device, many implants designed to be non-permanent are difficult to be removed and can cause multiple technical/safety problems. Therefore, effective processes to functionalize fixation elements in removable implants can represent a viable solution but they are still not studied appropriately. Available actual solutions include the possibility to leave the overall plate implanted or to use “ad hoc” methodologies to remove locked/damaged screws with a consequent high chance of damaging tissues. Retaining the implant not designed as permanent can potentially put the patient life at risk [6, 8]. It involves a series of drawbacks that cannot be neglected: it may compromise the mechanical strength of the bone by stress shielding, may cause soft tissues irritation, allergic reactions, risk of carcinogenesis, fractures due to stress peaks at the extremity of the plate, discomfort or pain [10, 11]. Nevertheless, a large number of elective orthopaedic procedures in occidental countries involve the implant removal surgery [12, 13] for which the indications for the operation and its estimated timing are controversial [14]. Thus, this paper proposes a functionalization technique able to significantly improve LCPs fixation screws to fulfil their requirements inhibiting, at the same time, direct osseointegration of the titanium part with the bone. The procedure involves laser ablation and a subsequent biopolymer coating by 3D bioprinting. The experimental results demonstrated the capability of the proposed methodology to successfully produce safe and improved titanium screws.

2. Materials and Methods

The material used for the experimental campaign is Ti6Al4V titanium alloy, in particular, both 1 mm thick sheets and maxillary fixation screws have been employed to execute the tests. It is

worth noting that this kind of fixation screw has been selected as the plate-related complications often occur during removal procedures due to the physical properties of facial tissues. Surface properties of the material, before and after laser irradiation, have been evaluated by means of several techniques, including Scanning Electron Microscopy (SEM), contact angle and surface roughness measurements. SEM analysis allows to assess the evolution of surface topography and crystal structure as a function of laser processing conditions. Contact angle provides a qualitative information on the effectiveness of the laser treatment to produce a surface with high wettability [3], while surface roughness can play a significant role on the coating strength and therefore needs to be determined [15]. After the blanking process, flat samples were electropolished (EP) using a Lectropol-5 (Struers) for 30 seconds with a voltage of 30 V and a flow rate equal to 12 ml/s. Thus, laser treatment was performed by using an air-cooled ytterbium fiber laser system (Lasit CompactMark G8) with 100 W maximum average power and 1065 nm wavelength. The laser had a maximum pulse frequency of about 1 MHz and the beam focused onto the surface by an F-theta lens (f = 160 mm) with a focus diameter of 55 μm. For the experimental campaign the scanning speed of the laser spot and the laser power were varied up to four levels each, while the line spacing (i.e., pitch) was set equal to the beam diameter so that the pulse frequency was accordingly calculated. The surface roughness and topography were determined using a non-contact white light confocal based profilometer (Rtec/UP-24) able to deliver high-resolution height profiles with a vertical resolution of 10 nm and equipped with a high-resolution camera. Surface roughness was measured from the raw signal by filtering the spatial frequency content according to the ISO 25178-2:2012. In particular, the arithmetical mean height (*Sa*), the maximum height (*Sz*), the reduced valley depth (*Svk*) the skewness (*Ssk)* and the kurtosis of height distribution *(Sku)* were determined at different area of the treated surface in order to have a statistically accurate dataset. The above roughness parameters have been selected since *Sa* and *Sz* are not sensitive to small changes in profile even though providing a good overall description of height variations. Therefore, other standard roughness parameters have been selected for the analysis providing a better surface description in terms of height distribution, sharpness of the profile and tendency to retain lubrication. The contact angle was analyzed by the sessile drop technique using a DSA30S (Krüss Scientific). Distilled water drops (3 μl) were placed on the titanium substrates to track the equilibrium contact angle as a function of the process parameters. The average of five measurements was determined in order to ensure the robustness of the results. Subsequently a 3D bioprinter (BioX, Cellink) has been used to coat the treated samples with a biocompatible polymer. In particular, a bioabsorbable polymer produced for human in vivo applications was used. It is a medical grade white semi-translucent gel, with an endotoxin level <0.5 EU/mL, pH 5.4-6.6/7.1-7.4, and viscosity of 2.1-5.0 kPa·s/0.9-1.4 Pa·s. $CaCl_2$ crosslinking agent is used with an endotoxin level <0.5 EU/mL, pH of 6.7-7.4. The bioabsorbable polymer was printed at room temperature as it can stand with little to no alterations to the printability. The applied extrusion pressure was set equal to 20 kPa for printing continuous filaments at a 10 mm/s printing speed. After printing, few drops of the crosslinking agent were placed over the polymer and left for 30 seconds before removing it with a micro pipette. The coated samples were then left to dry for 24 hours before testing. After coating, micro scratch tests have been performed using an Anton Paar micro-scratch tester with a Rockwell tip at a progressive load from 10 mN to 1000 mN, a length of 10 mm and averaged for three measurements. The test was used to determine the critical load for coating delamination thus assessing the coating adhesion. Furthermore, in order to clearly identify the area where the coating was completely removed from the substrate, SEM images were also taken after the test using an UHR-SEM ZEISS CrossBeam 350. The scratch test results, combined with roughness and contact angle were used to determine the most suitable laser parameters combination for treating the plate screws. After the coating, screws were tested at standard torque load in order to assess the biopolymer adhesion strength during screwing procedure. The overall results were assessed by analyzing the thread surface before and after the screws installation.

3. Results and discussion

3.1. Surface morphology and topography

SEM images of the laser treated surfaces, displayed in Fig. 1, show that laser irradiation enabled different extents of morphological modifications. All the selected parameters had an influence on surface topography. In particular, laser irradiation induced extended surface melting at the lowest scanning speed and higher laser power since the amount of energy increased. However, in order to distinguish the depth of the laser grooves by isolating the effect of multiple passes, a single-line laser treatment was also executed on flat samples and the overall depth was analyzed by means of an optical microscope and a profilometer (Fig. 2). The results confirmed the combined effect of scanning speed and power to produce deeper grooves on the titanium surface while, at increasing speed the overlap between two different laser spots is more evident since the local amount of energy decreases with a consequently reduced melted material around the spots. On the contrary, higher power leads to an increased melted area which turns into a deeper channel at lower speed and a less uniform groove boundary at higher speed.

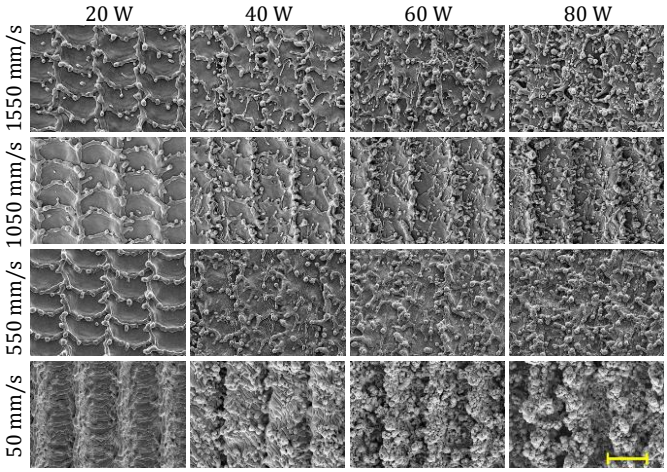


Figure 1. SEM images of laser treated Ti6Al4V substrates as a function of laser scanning speed and power (scale unit = 50 μm).

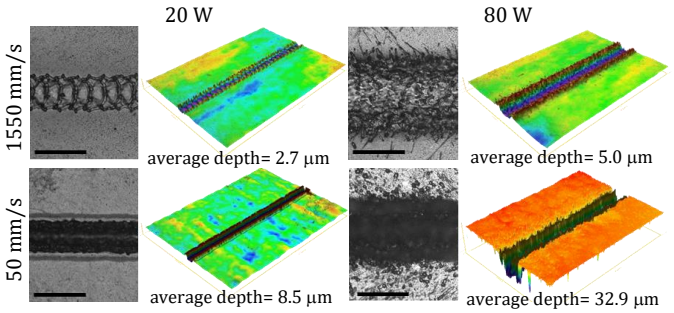


Figure 2. Microscope and surface profile for selected cases highlighting grooves depth reached at varying laser parameters (scale unit = 100 μm).

3.2. Surface roughness and wettability

The roughness trend shows a significant correlation between surface changes and laser irradiation. In detail, as shown in Fig. 3, the surface mean roughness and the arithmetical mean height always increase at lower scanning speed, highlighting the ability of the laser system to deliver a higher amount of energy enabling mechanical interlocking. However, the influence of the laser power is not clearly explained by *Sa* and *Sz*. In contrast, it significantly affects the *Svk*, especially when a lower scanning speed is applied. The reduced valley depth shows how the amount of melted material can fill the grooves, protruding through the boundary and reducing the valley depth when higher laser power is considered, as also confirmed by the results shown in Fig. 2. Skewness results also helped to better explain the phenomena occurring during laser ablation. In fact, it demonstrates that the combination of medium laser power and lower scanning speed leads to an overall surface with microchannels (low surface peaks and deep valleys) enabling more lubrication capacity of the surface as also confirmed by *Sku*. The latter points out how the medium amount of energy gives rise to a surface topography with high peaks and low valleys as for the efficiency in generating sharper grooves with a smaller amount of melted material. For the determination of the contact angle (CA), θ, as established by the measurement technique, the equilibrium contact angle has to be reached in order to measure its final value. Figure 4 reports the results for the EP (a) and the laser treated (LT) (b) specimens. In particular, the EP samples showed an average CA of 76° while it was not possible to reach a steady state condition for laser treated ones. Fully wettable surface within 3 seconds from the drop delivery was noticed for all the investigated process parameters which resulted onto superwicking surfaces: super wettable surfaces where no contact angle can be determined after the drop deposition.

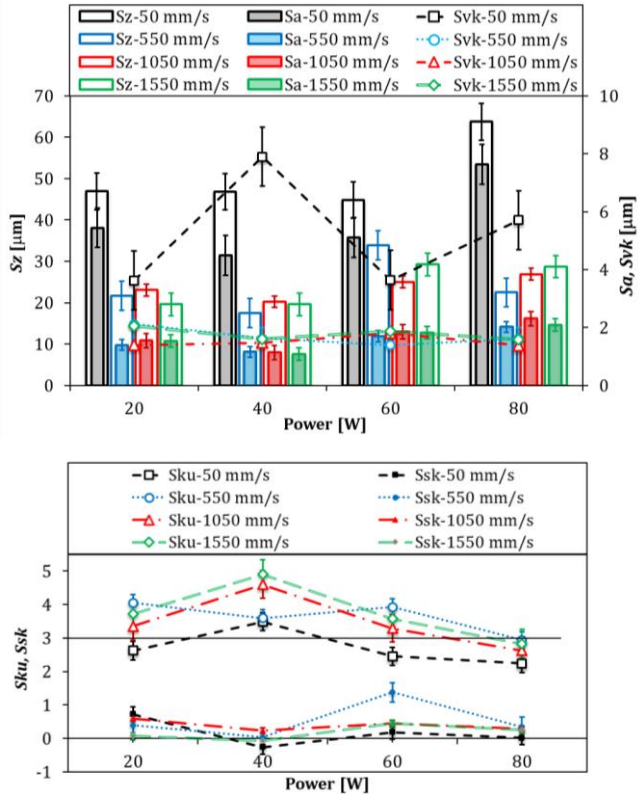


Figure 3. Surface roughness parameters measured for laser ablated surfaces (the error bars indicate standard deviation; for EP sample: *Sz* = 2.43 µm, *Sa* = 0.40 µm, *Svk* = 0.48 µm, *Sku* = 2.20 and *Ssk* = 0.17).

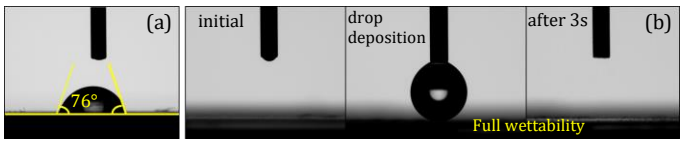


Figure 4. Contact angle measurement procedure and results for EP and laser treated surfaces.

The contact angle results were confirming the capability of the laser treatment to generate textures viable for dramatically tuning surface wettability. Combining wettability tests with roughness and morphological results, samples processed at 50 and 1550 mm/s were selected to exploit coating strength. Thus, eight parameters combination were sampled to be coated and tested. 3D bioprinter was then used to deposit the biomaterial over the substrates precisely delivering a 100 µm of biopolymer thickness on the selected surfaces.

3.3. Scratch test on coated samples

The test allowed to correlate the image of the scratched surface with the corresponding loading value identifying the critical load at which delamination of the coating occurs. As shown in Fig. 5, the biopolymer adhesion strength was significantly improved after laser treatment. Moreover, the scratch surface reported in Fig. 6, demonstrated that the delamination of the EP samples occurred significantly before the other laser treated samples. The critical load identified for the polished sample was measured to be 406 mN while the worst laser treated surface exhibited a critical load of 496 mN. As overall, the laser irradiation was able to successfully improve the coating strength especially at higher speeds. The latter result was attributed to *Sku* which exceeds the 3-value, i.e., sharp surfaces are obtained. However, given a critical load of 1000 mN, surfaces treated at 40 W showed no delamination of the coating. It is worth noting that the threshold value of the maximum load selected herein is significantly higher than the load found for biological coating Ti6Al4V for orthopaedic procedures [16]. Thus, in order to evaluate which surface treated at 40 W exhibits higher adhesion, further scratch tests were carried out increasing the maximum load up to 2000 mN.

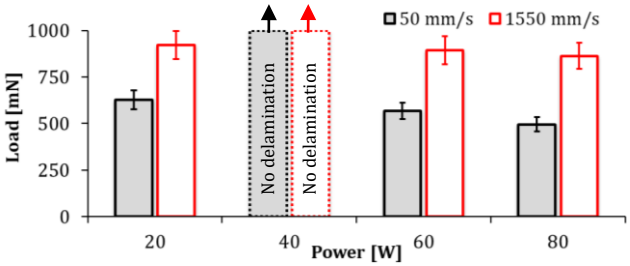


Figure 5. Critical load identified after scratch tests of laser treated surfaces at varying scanning speed and laser power (the error bars indicate standard deviation).

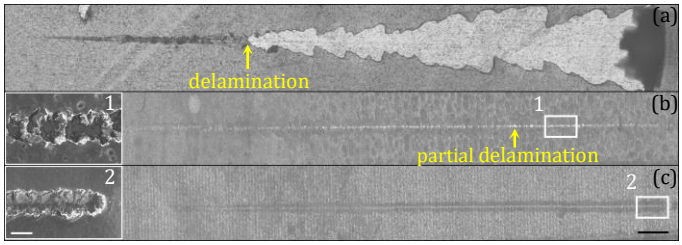


Figure 6. Micrographs and SEM images of EP (a), LT at 50 mm/s and 80 W (b) and LT at 50 mm/s and 40 W (c) samples after scratch tests (white scale bar = 100 µm, black scale bar = 500 µm).

Both treatments, i.e., 50 mm/s and 1550 mm/s, exhibit partial delamination starting from similar critical loads (1258 mN and 1207 mN for 50 mm/s and 1550 mm/s, respectively). Due to this evidence, it was not possible to select the best treatment only based on delamination results. Then, by considering the roughness results, it was found that both surfaces are characterized by similar *Sku* and *Ssk* values, while *Sa*, *Sz*, and *Svk* values are significantly higher for 50 mm/s treatments. Due to these overall evidences, laser treatment at 40 W and 50 mm/s was selected for treating fixation screws before coating.

3.4. Tightening test of maxillary plate fixation screws

Maxillomandibular fixation can be carried out with the help of arch bars, wiring, miniplates, microplates, 3D plates, etc. Different wiring techniques and plating systems require fixation screws. In this context, being able to optimize the screw reliability in terms of ease of removal is a key point. Thus, fixation screws were laser treated, coated and tested in order to assess the overall procedure effectiveness in fabricating advanced fixation screws for human applications. In particular, the 3D design of the screw was imported into the bioprinter software in order to execute coating following the titanium screw shape keeping its thickness constant along the overall threads. The critical torque force identified as the force where the coating delaminates from the screw was increased compared with that found for the untreated element. Furthermore, the force applied herein was comparable to the tightening load usually recommended for maxillomandibular and intermaxillary fixation screws (ranging from 0.2 to 0.4 Nm) [17]. In particular, an initial fixation torque equal to 0.2 Nm was selected for screw fixation which result in partial delamination for the untreated screw and no damage for the treated one. By increasing the torque force up to 0.25 Nm, the coating was completely removed from the untreated screw while the laser-treated one does not exhibit any visible damage. The textured screw exhibit coating detachment for fixation torque equal to 0.4 Nm. Figure 7 shows the overall test procedure for the untreated (a) and treated (b) screw. The lack of chemical bonding and mechanical interlocking for the as-received screw led to the sliding of the coating over the threads representing a critical issue during the surgical procedure. On the other hand, Fig. 7 also shows the effectiveness of textured surfaces in holding the polymer during screw tightening with a tremendous increase in delamination load exceeding the reference tightening torque forces. Yellow arrows indicate the first delamination sites for testing at standard torque force for the untreated screw and a 60% higher tightening force for the treated screw. The last picture in the sequence indicates the final delamination mechanism for both cases. It is worth pointing out that the critical value reached by the LT screw is 60% higher than the maximum allowed force for tightening standard screws.

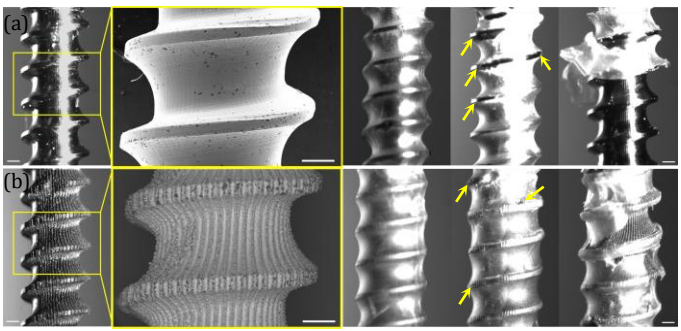


Figure 7. Untreated (a) and treated (b) screw before and after tightening test (scale bar = 500 μm).

4. Conclusions

The paper proposes an advanced functionalization and coating technique for producing high performance titanium fixation screws. In particular, the screw surface has been modified by laser ablation giving rise to a superwicking surface prone to successfully be coated by a bioabsorbable polymer which can be used as a sacrificial layer during the overall screw implantation time. The implemented procedure involves the use of a modern bioprinting technique that allows to fast and easily select the coating thickness to be applied in order to consider the specific period of screw implantation time relative to the absorption time of the biopolymer. Thus, the overall manufacturing procedure fits the requirements of highly flexible systems and customizable medical devices to dramatically improve the patient quality of life and reduce the risk of complications during removal surgery procedures for LCPs.

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