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Surface Characterization Of Ultra-Short Laser Textured Titanium For Biomedical Application

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Abstract

Surface modification is assuming a strategic role for interface properties tuning, either in the case of interaction between implant and tissue or substrate and coating. However, sometimes a lack of integration between a comprehensive implant surface characterization and, for instance, biological phenomena occurrence can be detected, dealing with inherently different fields of study. This work aims to provide a suitable approach that could allow correlation between substrate features and surrounding environment alterations, whether it biological or not. A chain of characterization techniques and their role within the research path will be explored employing a case study: biomedical *Ti6Al4V* titanium alloy treated with ultra-short laser for surface texturing and its features and interactions with a natural polymer-based composite as a potential coating.

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Keywords: Ti6Al4V; surface characterization; laser texturing.

1. Introduction

Surface represents the first interaction between components and surrounding environment. It controls their behavior not only with respect to corrosion and wear but also biological reactions, in case the part is in contact with tissues. In view of this, several surface modification techniques are being studied and implemented to modulate component resistance and biological response [1]. These techniques often involve mechanical, physical, chemical or biological alterations and can be used separately or in combination. In the broad range of available techniques, some of them involve material removal or displacement, most likely with simultaneous material modification, others involve material deposition.

As manufacturing and secondary processes represent the input, component quality is a result of the complex interactions within the production chain and it needs to be expressed in terms of function-related outputs.

Some of the parameters of interest for performance can be recognized in surface texture, composition, stiffness, charge and, as a direct consequence, wettability. Few of these, fall into the definition of surface integrity, introduced as condition of a surface produced by surface generation operations and often related to component response to aggressive environments [2].

In fact, mechanical failure together with corrosion and wear are related to microstructure, residual stresses, chemical species located on the surface and their stability but also

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surface overall shape and discontinuities which can bring to higher stresses and localized failure. [3]

Furthermore, it is acknowledged that cells and pathogens are sensitive to topographical features with which they interact and their chemical and mechanical nature [4, 5].

When it comes to the deposition of material over a substrate, both substrate and coating features dictate interface behavior and adhesion [6]. As a matter of fact, adhesion results as an interplay between mechanical, chemical and physical interactions between substrate and coating but also coating deposition technique, thickness, internal stresses and, clearly, working environment.

Thus, just as important as the technique employed for modification, a thorough characterization of the surface enables to identify possible factors affecting service performance. In this work, an overall view on surface layer features and their characterization will be provided and discussed on the basis of a case study.

2. Case Study

The presented case study concerns the interactions between a functionalized substrate and a potential coating: substrates of interest are in *Ti6Al4V* alloy while for the coating a chitosan-based one is studied. In fact, titanium alloys have major role in prostheses manufacturing and dentistry but, as most metallic alloys, they suffer from problems related to corrosion, potentially toxic ions release in the body, integration with contacting tissues [7].

These drawbacks could be balanced by introducing a coating, thus preserving mechanical properties of the overall biomedical device and tuning local surface properties towards an improved tissue-implant interaction [8].

But, as previously mentioned, coating adhesion to a substrate is influenced by several factors and, having chitosan poor adhesion to metallic substrates [9], a simultaneous modification of substrate chemical and topographical properties is one of the keys to proper interface bonding.

Within this context, laser texturing is considered a viable processing technique, as it gives a certain flexibility in the creation of peculiar surface topographies and high production rate, thus can be easily applied within the industrial context, but it also enables modification of surface reactivity [10].

Textures have been created on polished discs employing a 10W picosecond IR laser source (1064 nm wavelength) with attenuated power, below 1W. The two structures consist of grids made up of pillars and wobbles, respectively. Polished samples have been taken as a reference.

3. Methodology

As widely acknowledged, surfaces can be characterized based on (i) texture, including macro- micro- roughness, direction of the dominant pattern, defects; (ii) microstructure and deformed surface layers as a result of processing; (iii) nature of chemically reacted, chemisorbed and physisorbed layers [11].

For surface texture, Confovis structured light profilometer connected to a Nikon Eclipse LV150N microscope was employed to obtain 3D maps of areas of interest for each type of sample. The analysis was supported by SEM imaging (ESEM Quanta-200 - Fei Oxford Instruments).

Surface composition has been analyzed through the combination of EDS (X-EDS Oxford INCA-350) analysis supported by Raman spectroscopy (LabRam - Jobin-Yvon) employing a 532 nm wavelength and 40 mW power laser, performing 3 replications for each scan, each of 10 s duration, in the region 100 - 1600 cm^{-1}.

Samples have been cross-sectioned, polished up to a 0.5 µm grade and analyzed after chemical etching with Kroll's reagent to evaluate microstructural variations and altered layer. The analysis was supported by Berkovich nanoindentation along sample thickness (NH^2 CSM Nanoindentation Platform – Anton Paar) with 50 mN maximum load, 10 s holding time, 10 repetitions per depth value.

Apparent static contact angle variations due to processing have been assessed through the sessile drop technique (DSA30S – Kruss Scientific) in standard laboratory environment for different times after deposition, employing chitosan-based solution made up of 0.7% of chitosan in 1% acetic acid mixed with 0.3% 77S bioactive glass nanoparticles, delivering on substrate surfaces 1 µl of solution and performing 5 repetitions. Surfaces were previously sonicated in absolute ethanol and distilled water to remove contaminants.

4. Results and Discussion

4.1. Texture analysis

Textures generated through laser, as reported above, are made up of: (i) protruding squared pillars left by laser material removal to create grid-like channels (laser textured grid – LTG) in Fig. 1a, (ii) squared slots generated from material removal, arranged in a grid-like layout (laser textured wobbles – LTW) in Fig. 1b. Both types of surfaces are characterized by a hierarchy of micro- to nano- features, the former consisting in the features explained above, the latter made up of laser-induced periodic surface structures (LIPSS) shown in magnifications of Fig. 1c and d.

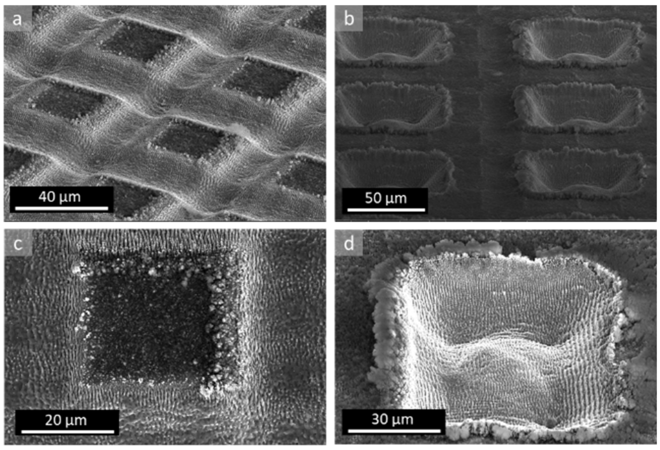

Fig. 1. Tilted SEM images of studied surface structures (a)(c) laser textured grid; (b)(d) laser textured wobble.

3D maps of studied surfaces are reported in Fig. 2, respectively polished reference (P), LTG and LTW while main surface parameters according to ISO 25178 are reported in Table 1. It is immediately noticeable how *Sa*, *Sq*, *Sz* and *Ssk* stay in the same order of magnitude for both textured samples while differences in *Ssk* values highlight how the probability to find surface above the mean line is higher for LTW.

Table 1. Surface roughness values for studied samples.

Parameter	LTG	LTW	P
Arithmetic mean height – *Sa* [µm]	2.22	3.48	0.05
Root mean square height – *Sq* [µm]	2.76	4.21	0.06
Maximum height – *Sz* [µm]	14.82	20.22	2.53
Skewness – *Ssk* [-]	-0.07	-1.28	-0.67
Kurtosis – *Sku* [-]	2.57	3.27	11.97

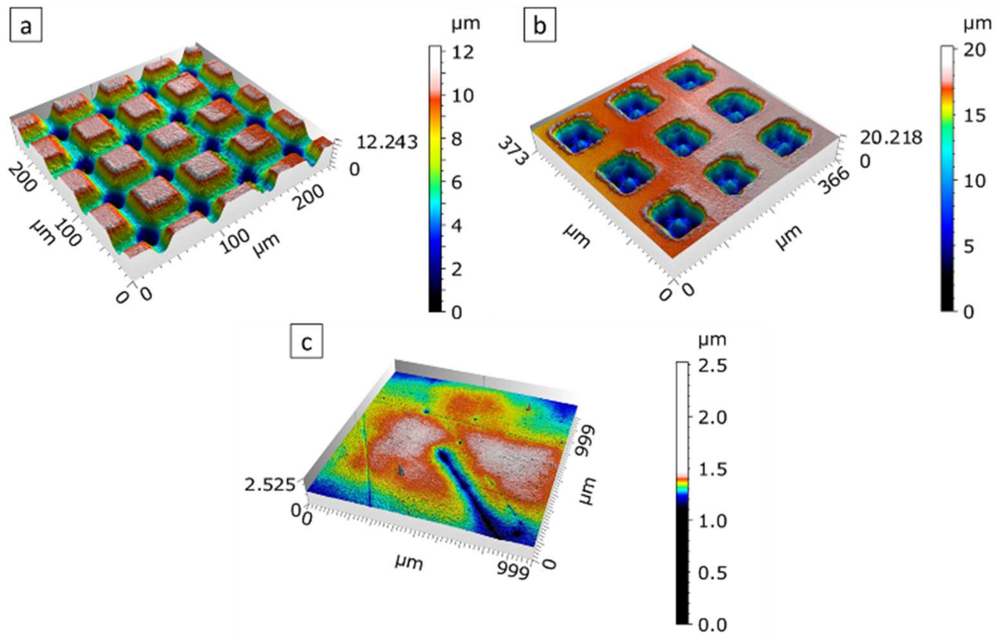

Fig. 2. 3D maps from confocal profilometry (a) LTG; (b) LTW; (c) P.

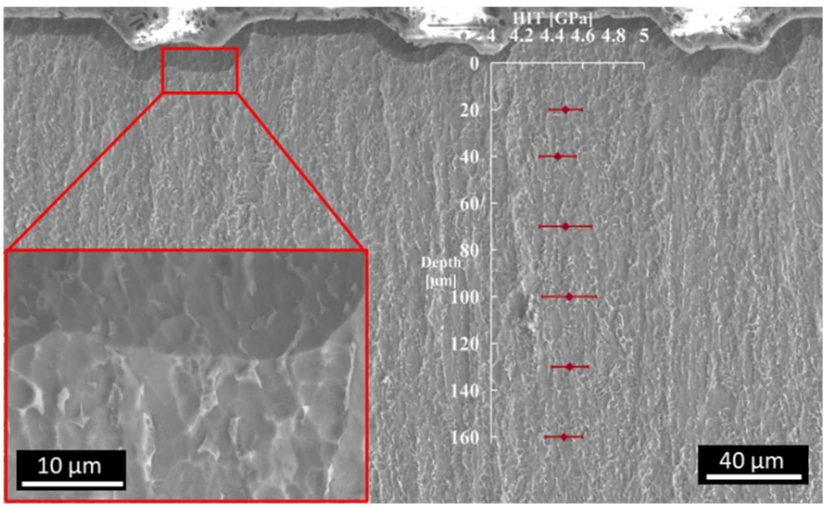

Fig. 3. Microstructure and nanoindentation hardness along the cross-section of LTW sample.

4.2. Microstructural and spectroscopic analysis

The core concept of ultrashort laser modification is the reduced impact of the treatment on microstructure and composition, which can be expressed in terms of reduced affected zone [12] in the order of few microns below the surface. Figure 3 represents the cross-section of an etched LTW sample together with the plot of nanoindentation hardness (HIT) for varying depth below the surface: from the analysis performed, a confirmation of the above can be provided as no significant microstructural alterations have been detected along the depth below treated surface, according to the resolution of employed techniques; the same applies for LTG samples.

As regards surface composition after processing, no significant variations in terms of surface oxides formation have been found between laser textured samples and polished ones, apart from detectable presence of rutile (Fig. 4) on specific areas which were not directly subject to laser beam crossing but suffer from edge effects due to treatment.

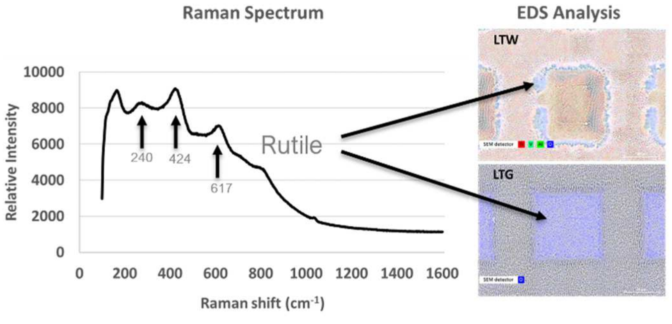

Fig. 4. Results from Raman and Energy Dispersive Spectroscopy on LTW and LTG samples.

4.3. Contact angle measurement

From the measurement of static contact angle, employing the chitosan-based solution, it has been found, as reasonably expected, an anisotropy in drop shapes (Fig. 5) which tend to follow pattern arrangement, on both laser textured samples. The same did not happen on the reference polished one, which showed isotropy in contact angle. Contact angles referred to 1 s, 5 s and 30 s after drop deposition are reported in Fig. 5. For LTG and LTW, images are referred to a measurement in parallel direction with respect to grid-like arrangement.

Few observations can be made: (i) under the tested conditions, *Ti6Al4V* tends to have hydrophilic behavior, as contact angle tends to always assume values below 90°; (ii) in case of laser textured samples the evolution of contact angle is faster with respect to reference; (iii) LTG and LTW have opposite behavior as the former tends to have higher contact angles while for LTW drops spread more easily and rapidly. Nevertheless, due to drop anisotropy, it is advisable to address the comparison for qualitative purposes.

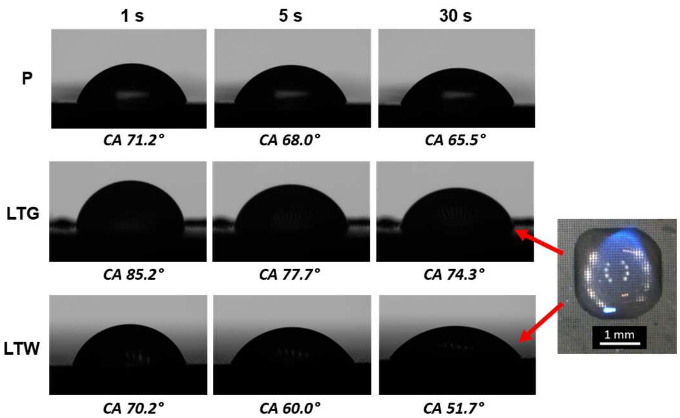

Fig. 5. Static contact angle for P, LTG and LTW samples for different times after drop deposition and anisotropy in drop shape for LT ones.

5. Discussion and Conclusions

Laser surface treatment clearly affected wettability of tested samples with respect to polished reference, acting on both surface topography for an improved mechanical interlocking of coating and substrate and local chemical composition, without introducing significant changes in microstructural properties of the substrate. Apart from the mechanical effect, the local presence of higher percentages of chemically active titanium oxide, if properly exploited, can enhance chemical polymer-metal bonding. Wettability is largely employed as an indicator of viable performance of coated samples [13], but it only represents one of the many acting factors and is itself affected by both topography and chemistry. Deposition process and, with it, coating solution penetration and stresses generated at the interface affect wettability regime and its final performance, as well as coating thickness and working environment.

According to literature, micron-sized topography plays a main role in affecting static contact angle while nano-sized one, as LIPSS, is responsible for contact angle hysteresis [14], thus their influence was not addressed in this study but will be subject of supplementary investigations, also in view of other phenomena, also biological, to be considered.

Thus, if on the one hand the tested structures might enable tuning hydrophilicity of substrates, the final substrate-coating system performance will be a result of the complex interaction of many factors and needs to be addressed with further experimental campaign.

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References

[1] Ratner BD, Hoffman AS, Schoen FJ, Lemons JE, Biomaterials science: an introduction to materials in medicine, 2004.

[2] Jawahir IS, Brinksmeier E, M'Saoubi R, Aspinwall DK, Outeiro JC, Meyer D, Umbrello D, Jayal AD, Surface integrity in material removal processes: Recent advances. CIRP Ann - Manuf Technol 2011 ; 60: 603–626. https://doi.org/10.1016/j.cirp.2011.05.002.

[3] Ashby MF, Jones DRH, Engineering Materials 1: An Introduction to Properties, Applications, and Design, 2012.

[4] Chang H-I, Wang Y, Cell Responses to Surface and Architecture of Tissue Engineering Scaffolds. Regen Med Tissue Eng - Cells Biomater 2011. https://doi.org/10.5772/21983.

[5] Zheng S, Bawazir M, Dhall A, Kim HE, He L, Heo J, Hwang G, Implication of Surface Properties, Bacterial Motility, and Hydrodynamic Conditions on Bacterial Surface Sensing and Their Initial Adhesion. Front Bioeng Biotechnol 2021 ; 9: 1–22. https://doi.org/10.3389/fbioe.2021.643722.

[6] Menčík J, Mechanics of Components with Treated or Coated Surfaces, 1st ed., Springer, Dordrecht, 1996. https://doi.org/https://doi.org/10.1007/978-94-015-8690-0.

[7] Yao Z, Lin TH, Pajarinen J, Sato T, Goodman S, Host Response to Orthopedic Implants (Metals and Plastics), Elsevier Inc., 2015. https://doi.org/10.1016/B978-0-12-800196-7.00012-8.

[8] Nobles KP, Janorkar A V., Williamson RS, Surface modifications to enhance osseointegration–Resulting material properties and biological responses. J Biomed Mater Res - Part B Appl Biomater 2021 1–15. https://doi.org/10.1002/jbm.b.34835.

[9] Leedy MR, Martin HJ, Norowski PA, Jennings JA, Haggard WO, Bumgardner JD, Use of chitosan as a bioactive implant coating for bone-implant applications. Adv Polym Sci 2011 ; 244: 129–166. https://doi.org/10.1007/12_2011_115.

[10] Samanta A, Wang Q, Shaw SK, Ding H, Roles of chemistry modification for laser textured metal alloys to achieve extreme surface wetting behaviors. Mater Des 2020 ; 192:. https://doi.org/10.1016/j.matdes.2020.108744.

[11] Bhushan B, Introduction to tribology, second edi, John Wiley & Sons, Ltd., 2013.

[12] Kong MC, Wang J, Surface quality analysis of titanium and nickel-based alloys using picosecond laser. Procedia CIRP 2014 ; 13: 417–422. https://doi.org/10.1016/j.procir.2014.04.071.

[13] Rotella G, Orazi L, Alfano M, Candamano S, Gnilitskyi I, Innovative high-speed femtosecond laser nano-patterning for improved adhesive bonding of Ti6Al4V titanium alloy. CIRP J Manuf Sci Technol 2017 ; 18: 101–106. https://doi.org/10.1016/j.cirpj.2016.10.003.

[14] Lößlein SM, Mücklich F, Grützmacher PG, Topography versus chemistry – How can we control surface wetting? J Colloid Interface Sci 2022 ; 609: 645–656. https://doi.org/10.1016/j.jcis.2021.11.071.