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*Article*

# Nanosecond Pulsed Laser Irradiation of Titanium Alloy Substrate: Effects of Periodic Patterned Topography on the Optical Properties of Colorizing Surfaces

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**Abstract:** Surface treatments of metals based on laser marking technology is an important application in a wide range of industrial fields. By specific combinations of laser processing parameters, the modified surface leads to different textures with specific roughness and colored appearance. Most of current works are focused on the modification of color tonality of flat surfaces, or the development of specific topography features, but the combination of both processes is not usually evaluated, mainly due to the complexity to control the optical properties on rough surfaces. This research presents an analysis of the influence of the micro-geometrical characteristics of periodic patterned laser tracks on the chromaticity and reflectance of Ti6Al4V substrates. The samples were irradiated with an infrared nanosecond pulsed laser under air atmosphere, taking as control parameter the scan speed of the beam. A roughness evaluation, microscopic inspection, absorption and chromaticity examination were conducted. Although micro-crack growth was detected in isolated case (10 mm/s), the possibility of adjusting the result color were demonstrated by controlling the thermal affected zone thickness of the textures. Results of rough/colored combined textures allow opening new perspectives in industrial design, particularly in aesthetic applications with special properties.

**Keywords:** Titanium, laser marking; color; reflectance; roughness; oxidation.

## 1. Introduction

Surface texturing has recently acquired an important growth in engineering applications, resulting in significant improvements in load capacity, wear resistance and friction coefficient of tribo-mechanical parts. Under tribological conditions, texturing geometries remove wear debris from the sliding track, reducing the involved abrasive effects of these hard particles, and also acting as lubricant reservoirs [1-2].

Among the several techniques that can be applied for texturing (micro-drilling, mechanical indentation, electro-discharge texturing, etc), Laser Surface Texturing (LST) has shown some relevant advantages regarding chemical and mechanical processes. On the one hand, the laser system can be adapted to a wide range of parameters, become a faster and more flexible method than machining operations. On the other hand, these treatments are usually based on laser irradiation processes

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under air atmosphere, avoiding the use of lubricants or coolant fluids that is necessary in some machining processes [3].

Therefore, LST is considered as a viable process for surface engineering, contributing to the development of functionalisation of components [4]. Also contributes to the development of sustainable manufacturing by means of an environmentally friendly process, in comparison to chemical and conventional machining [5-6].

Ti6Al4V is a well-known α+β (grade 5) Ti-based alloy, widely used for the manufacturing of aerospace parts and biomedical components, mainly due to their good weight/mechanical properties ratio, high corrosion resistance and excellent biocompatibility.

The ability to maintain control over the main mechanical properties on the surface of this alloy by LST can produce several benefits. In the healthcare sector, the biocompatibility and biomechanical behavior are key factors, as well as the improvement of the sliding features under biological fluids [7-8]. In the case of strategic alloys for the aerospace industry, surface modification treatments are used to overcome material limitations and to improve its functional performance [9-11].

In the case of Ti6Al4V alloy, the use of LST is focused to overcome these functioning limitations, such as poor wear behavior. The unstable frictional response of titanium alloys, coupled with severe wear behavior under certain rubbing conditions, make the use of this type of alloys difficult to apply in severe tribological applications [12-13].

Moreover, the exposure of this alloy to a LST treatment in an air atmosphere -favored by a local increase of temperature- causes the combination of the external surface layer with the oxygen present [14], giving rise to the development of a thin protective layer composed by titanium oxides, mainly in rutile (TiO2) form [15-16].

After oxidation phenomena, transparent oxide films on a reflecting substrate give rise to color. So, titanium substrate reacts changing the initial tonality to a color range mainly related to the thickness of the oxide layer and the conditions of the thermal treatment [17-18].

A wide range of color tonalities can be achieved by modifying the main control parameters of the LST process in Ti6Al4V, according to variables such as thickness and microstructure of the oxidation layer [19].

This property, the color, can be considered as aesthetic or non-functional regarding to the advantages that can provide the LST process, but can be also considered as an easy indicator of the characteristics of the treated surface. A kind of color can determine a surface characteristic. Also, by modifying parameters during the LST process, it could be obtained textures with color variations, such as the color laser marking in steels [20].

There are several studies in the scientific literature that report on the LST of the Ti6Al4V alloy, mainly focused on the characterization of micro-geometry and the study of the relationship with tribological behavior, generally evaluated by studying the wettability and surface roughness [2,4,6, 21-22].

There are also some works that relate the influence of LST parameters on the color of textured surfaces, mainly by evaluating the optical properties (n, k) of oxide films by using spectrophotometry and ellipsometry techniques [23-28]. These measurements are useful for calculating the spectral reflectance, and can then be compared with the data measured by a spectroscope. The appearance of these titanium laser-grown oxide coatings is described by chromaticity, a standard by which these identifiers can be compared [29,30].

However, a lake of knowledge has been detected in the scientific literature about the study of color / mechanical properties and process parameters.

In this paper, a study of the chromatic changes -in terms of optical reflectance and chromaticity- and its relationship with the micro-geometrical variations -in terms of roughness-, is reported. LST parameters in the texturing of Ti6Al4V is key for the control of the surface morphology, that can be directly linked with the chromatic state.

## 2. Materials and Methods

### *2.1. Laser texturing process*

Ti6Al4V titanium alloy (UNS R56400) 50 mm x 50 mm plates with 5 mm thickness were cleaned by ether-petroleum/ethanol 50% dissolution. This plates were conditioned by mechanical polishing to an initial surface roughness of Ra<0.05 µm and Rz<0.15 µm. Ti6Al4V chemical composition (wt%) is shown in table 1.

**Table 1.** Ti6Al4V substrate composition (wt%)

| Al | V | Fe | C | O | N | H | Ti |
|---|---|---|---|---|---|---|---|
| 6.26 | 3.91 | 0.18 | 0.011 | < 0.10 | < 0.10 | < 0.10 | Rest |

The laser exposure was performed under room air atmosphere, using a commercially marking machine (ROFIN-SINAR Technologies Inc., Plymouth, MI, USA) based on a 10 W Ytterbium fiber infrared laser system with $\lambda = 1070 \pm 5$ nm wavelength, which generates pulses of $\tau = 100$ ns duration at repetition rate of $f = 50$ kHz. The laser spot with a focal diameter of $d = 60$ µm was moved over the surface of the sample with a scanning speed (Vs) range from 10 to 300 mm/s. Texturing process was developed through bidirectional parallel lines with a 0.1 mm distance between laser tracks. Textured areas over Ti6Al4V substrate consists of 10 mm x 10 mm size squares.

To evaluate the influence of laser processing parameters on the variation of the properties and features of the modified surfaces, the scanning speed of the beam ($V_s$) was taken as control parameter. Under this assumption, a single energy density of pulse/fluence ($E_d$) was chosen for the experimental tests, combined with nine different values of Vs, which are shown in table 2.

**Table 2.** Laser processing parameters

| Nominal Power (W) | Pulse rate (KHz) | $E_d$ (J/cm$^2$) | $V_s$ (mm/s) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 | 50 | 7.07 | 10 | 25 | 50 | 75 | 100 | 150 | 200 | 250 | 300 |

### *2.2. Evaluation methods*

Textured samples were subjected to two different types of analysis, on the one hand, through the chromatic changes, and on the other hand through the micro-geometrical variations, in terms of roughness, all induced by the laser treatments.

Color modification of the surfaces was evaluated by measuring the optical reflectance of the samples, using a dispersive spectrophotometer (Agilent, model Cary 5000) along with a 150 mm diameter integrating sphere accessory. Optical geometries 8º/di and 8º/de were used for color measurements, following the recommendations of the CIE (Commission Internationale de L'Eclairage) [31] Light reflectance values (LRV) of the textured surfaces were determined following the recommendations of the British Standard [32].

For the study of micro-geometrical characteristics of the textures, a roughness measure device Mahr Perthometer Concept PGK120 (Mahr technology, Göttingen, Germany).

Surface finish features were described by the roughness parameters of asymmetry or skewness (Rsk) and sharpness of the asperity peaks of kurtosis (Rku). These parameters, which are extracted from the Amplitude Distribution Curve (ADF), can provide a valuable information about the shape of the laser tracks shape.

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$$Rsk = \frac{1}{Rq^3}\left[\frac{1}{lr}\int_0^{lr} Z^3(x)dx\right] \quad (1)$$

$$Rku = \frac{1}{Rq^4}\left[\frac{1}{lr}\int_0^{lr} Z^4(x)dx\right] \quad (2)$$

Being $Rq$ a parameter that defines the root mean square roughness of the profile ordinates ($Z$) on the evaluation length ($lr$) [33]:

$$Rq = \sqrt{\frac{1}{lr}\int_0^{lr} Z^2(x)\,dx} \quad (3)$$

In addition to roughness characterization, laser tracks morphology and crack growth were studied on cross-section of the grooves by means of optical and scanning electron microscopy methods. The influence of the laser processing parameters on the development of modified texturized layers were evaluated by the measuring of hardness from the outer edge of the track. Under this consideration, the presence of oxidation phenomena, highly related with variations in color and hardness, was analyzed by using energy dispersive X-Ray spectroscopy (EDX).

## 3. Results and discussion

Laser texturing processes on the surface performs relevant modifications from the initial features of the substrate. The main alterations on the substrate can be related to micro-geometrical changes of the surface and color tonality variations of the samples. Because of the energy incidence of the laser along the paths used for this study, a material phenomenon occurs, giving place to the development of a linear parallel pattern of grooves on the substrate. Laser tracks show specific combinations of shape and size as a function of the processing parameters. In the same way, microstructural and chemical composition variations are modified in closest areas of the tracks, changing the initial properties of the titanium alloy. These kind of modification can be easily detected due to color tonality variations.

### *3.1. Micro-geometrical morphology of the laser textures*

In addition to the color variation, the modified samples show a substrate removal process from the laser tracks. These removal process results on the development of a linear parallel pattern texture. However, the use of different processing parameters may induce a wide range of shape and size of the grooves.

Taking as reference the scanning speed of the beam, a decrease of the grooves depth as a function of Vs was detected. Affected Ti6Al4V debris deposited on the upper area of the tracks were noticed, making that the density chart shows two clearly differentiated areas of material, Fig. 1. The analysis of the Rsk and Rku parameters show significant differences between low, medium and high Vs ranges.

For lower scanning speed, an increase trend was detected on each roughness studied parameters. Based on the interpretation of the ISO 4287 and ASME B46.1 standard, higher values of Rsk>0 implies that the laser tracks maintain greater volume of material below the midline of the profile, which is understood as larger grooves caused by more aggressive treatments. For Rku parameter, an increase trend with values greater than 3 are indicative of a sharp profile, confirming the existence of deep and narrow textures.

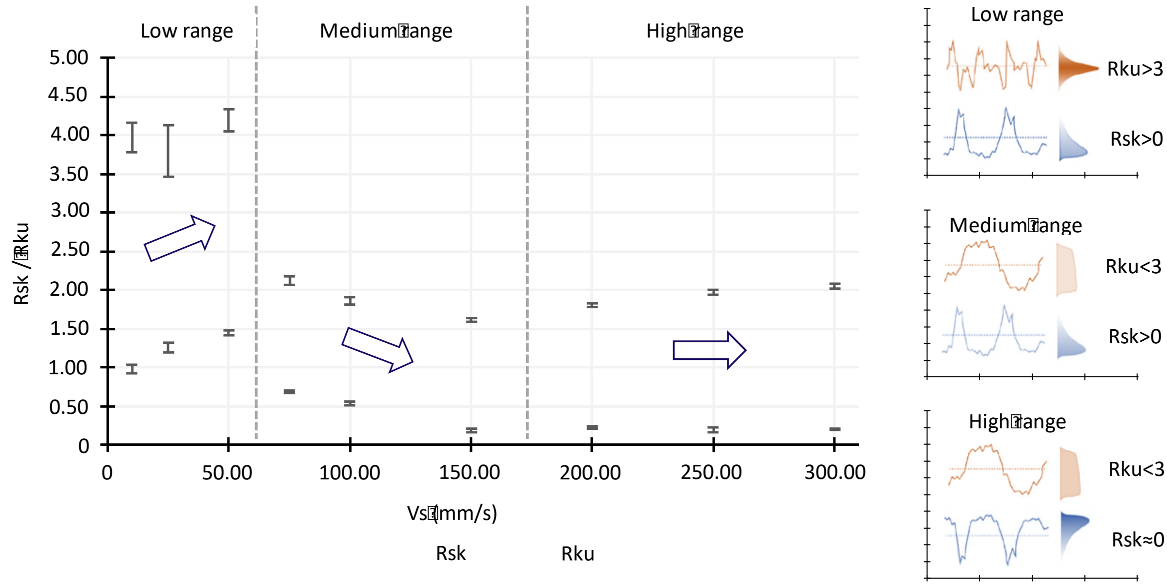
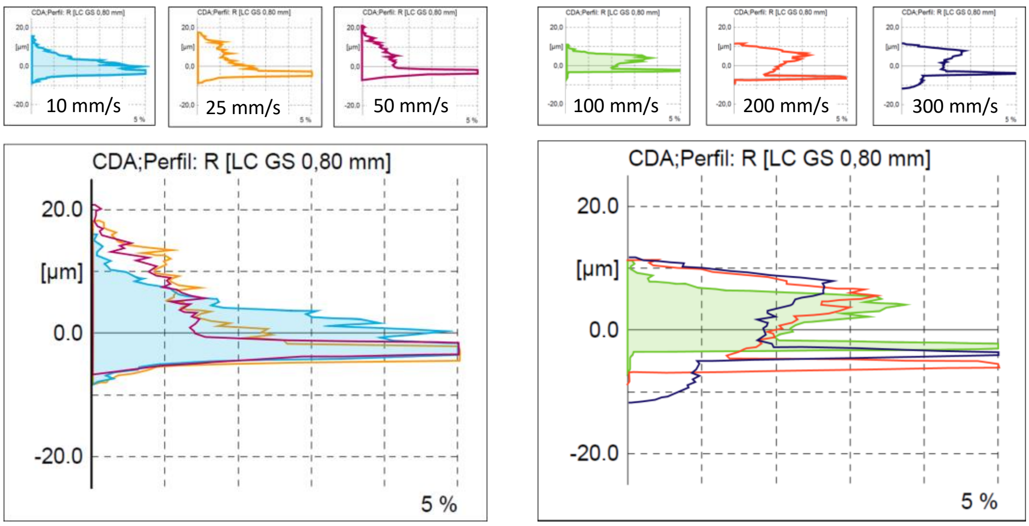



**Figure 1.** ISO 4287 Rsk and Rku behavior as a function of Vs

Medium Vs ranges (75-150 mm/s) involve a decrease in the values of Rsk and Rku. This fact results in softer asperities caused by the laser beam, and lower deep of the tracks. From these Vs range, some material debris detachment can be observed on the closest areas of the grooves.

The use of high ranges of Vs (200-300 mm/s) reduces the intensity of the treatments, giving rise to softer textures with low deep semicircular tracks. These treatments promote the uniform behavior of the roughness values, with Rsk < 0.5 and Rku < 2.

The analysis of the probability density function (Adf) from the material ratio curve (BAC) of the measured profiles reveals the existence of two different curves based on the shape and size of the textures. On the one hand, from lower scanning speeds (10-50 mm/s), the BAC curve shows a single maximum in the Adf located in the midline of the roughness profile. Furthermore, when Vs increases, a displacement of the material below the midline was detected, as illustrated in Fig. 2a. On the other hand, Vs ranges from 100 mm/s to 300 mm/s results in the generation of specific distributions, showing two maxima in the Adf located on both sides of the midline of the roughness profile, Fig. 2b.




(a) (b)

**Figure 2**. Different behaviors on probability density function as a function of Vs

In addition to micro-geometrical modifications in terms of roughness, the LST treatments, may induce microstructure variations and oxidative phenomena on the modified layer.

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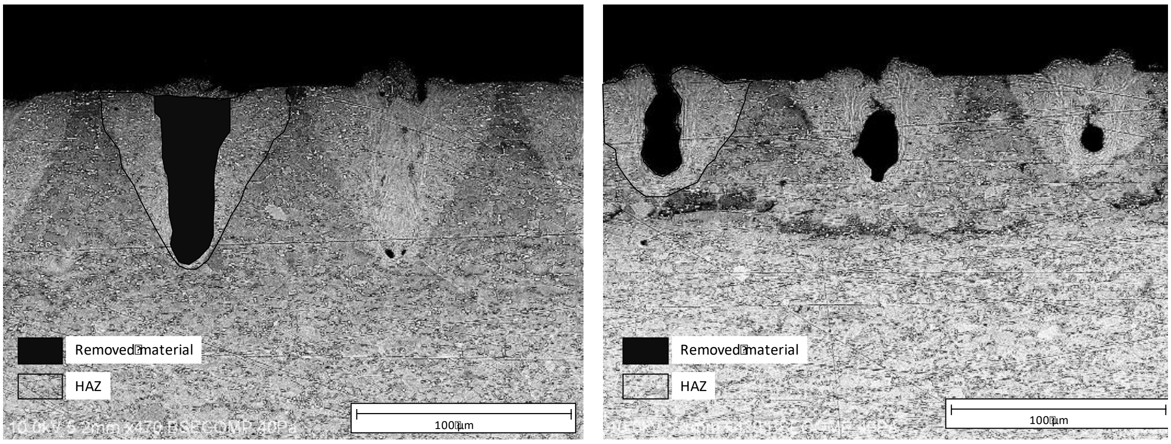
### *3.2. Influence of LST on thermal affected zone and microstructure*

As a consequence of the texturing process on the surface of the Ti6Al4V, microstructural changes were caused. A rapid temperature increase focused on small areas, and cooling processes in laboratory atmosphere, may affect the initial structure of the alloy. Furthermore, the development of the LST processes under room air atmosphere induce the presence of oxidative phenomena on the Heat Affected Zone (HAZ).

The Ti6Al4V (UNS R56400) alloy used for this research shows an α+β equiaxed microstructure. However, the surface treatment and the introduction of oxygen (as a α-phase stabilized element) results in significant changes on the microstructure and mechanical properties of the alloy. As can be seen in the figure 3, the HAZ close to the textures tracks is highly influenced by the intensity of the treatment, quantified by the Vs.

As described, the HAZ shows an important dependence to the scanning speed of the beam. The increase of the Vs implies that the beam remains less time over the same section of the alloy, giving rise to reduced tracks and consequently decreasing the HAZ, according to [15, 34], Fig 4.




(a) (b)

**Figure 3.** Heat Affected Zone of textured tracks (a) 50 mm/s; (b) 75 mm/s

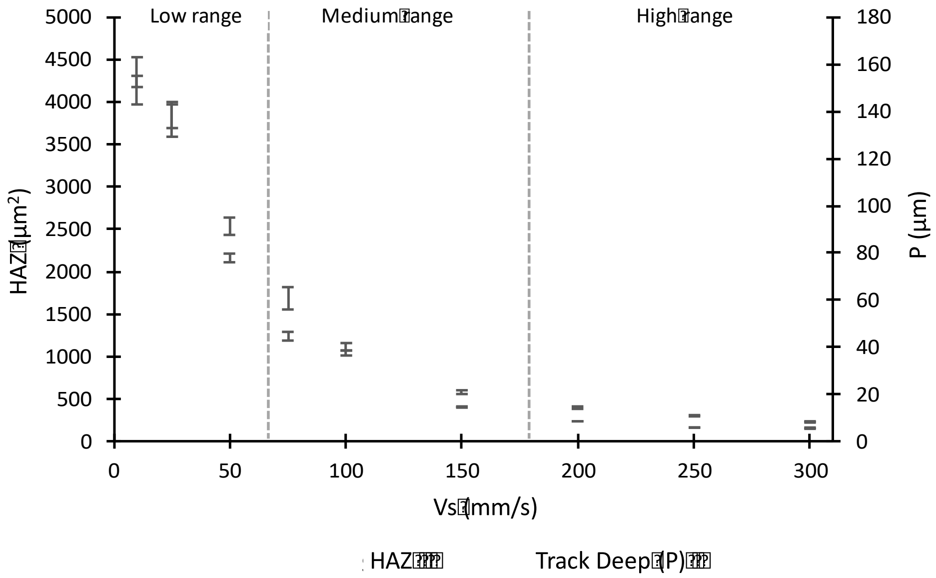



**Figure 4.** Thermal affected zone and laser tracks deep as a function of Vs

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Regarding to the microstructural modification, the rapid cooling process of the treated areas, may be the main cause to the transformation from a equiaxed grains of a $\alpha$+β to martensitic structures with laminar shape grains near to $\alpha$ phase, Fig. 5 [36].

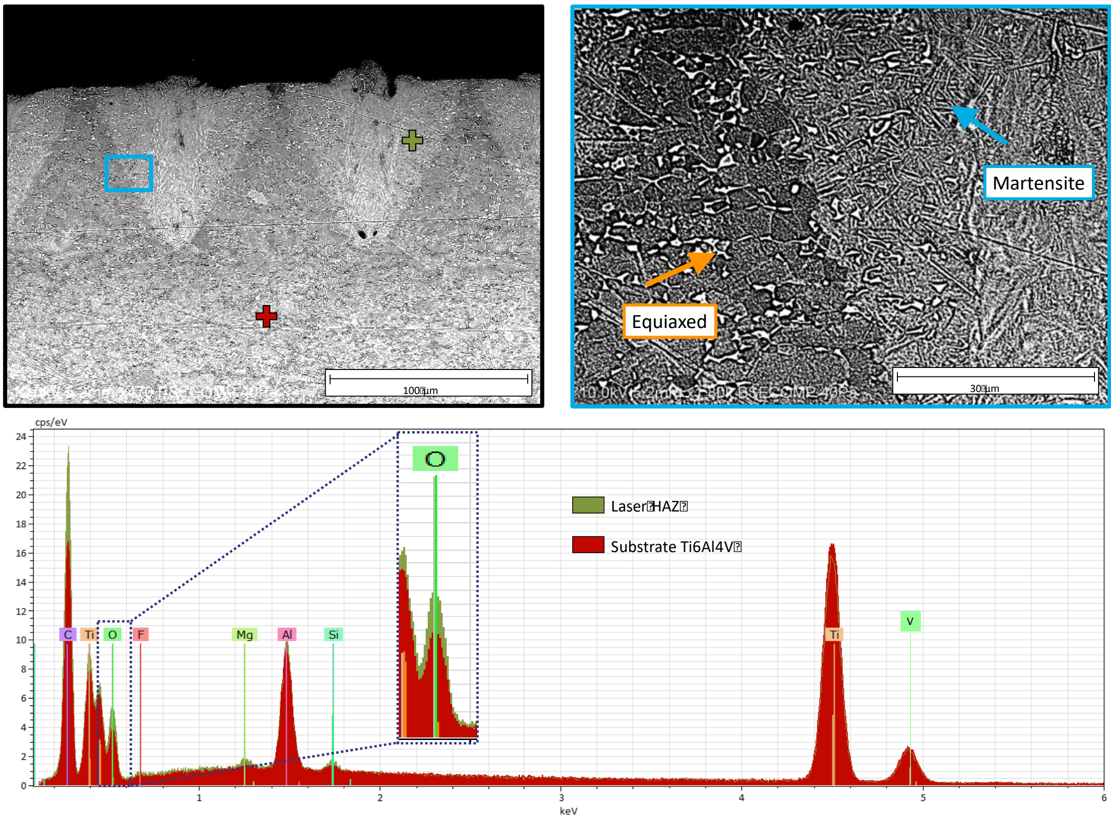


**Figure 5.** Microstructural and composition changes induced by laser treatment (Vs = 50 mm/s)

One of the most representative effect -in addition to the martensitic transformation- is the appearance of oxidative phenomena, mainly due to the increase of the temperature under air atmosphere, in which oxygen may enrich the composition of the modified layer.

### *3.3. Hardness variation and crack growth on textured surfaces*

An increment in the oxygen composition from the thermal oxidation, and the phase evolution to martensitic structure, makes possible the increase of the hardness of the modified layer. By the study of the hardness from the edge of the tracks, a direct relationship can be observed between the scanning speed of the beam and the increase of hardness on the thermal affected area. Under this consideration, the use of very low scanning speed (10 mm/s) results in the best results, in terms of penetration ability of the treatment. Taking as a reference the hardness of the untreated substrate (Ti6Al4V) with a nominal value of approximately 349 HV, by means of the laser surface treatments, a textured layer was obtained with a new hardness value more than four times higher than the initial one, Fig. 6.

Using the high performance conditions for the hardness increasing (Vs = 10 mm/s), a maximum penetration range of 60 µm was determined through the measurement results to obtain significant mechanical improvements. Under this thickness, the laser treatment for this purpose may not be an effective mean. On the other hand, mainly due to the cooling processes, in rare cases the existence of micro-cracks may occur, Fig. 6, according to [35]. Crack growth over the track surface is caused to the solidification process of the vaporized titanium alloy and the oxidation that takes place during the beam displacement.

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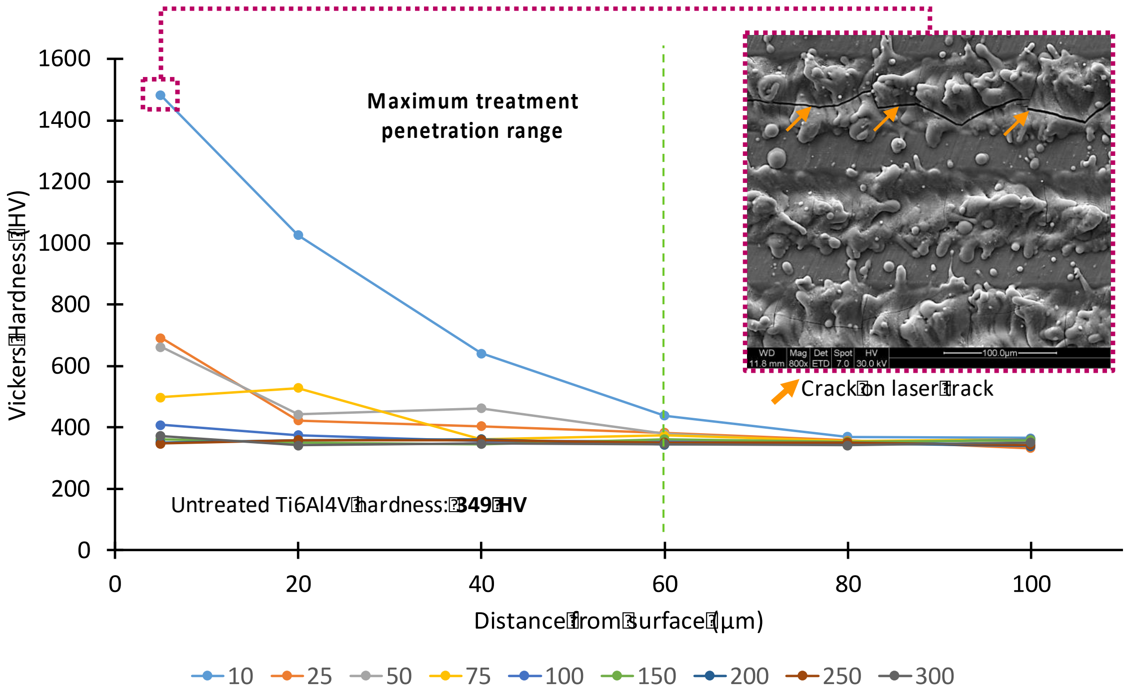


**Figure 6.** Hardness variation based on Vs and detail of micro-crack on laser track

*3.4. Color tonality variation of laser textured surfaces*

Laser radiation treatments may affect both the micro-geometrical topography and the physicochemical properties of the surface. One of the most representative effect of the laser texturing process on the Ti6Al4V surface may be the color tonality variation. Under oxidation phenomena, the titanium substrate reacts changing the initial tonality to a color range mainly related to the thickness of the oxide layer and the conditions of the thermal treatment.

When the tonality variations in the textures were analyzed, a sample color dependency was detected on the scanning speed of the beam. Under the range of Vs used, a color palette with golden and near blue tones were developed, fig. 7. As it was detected for previous parameters, the existence of three different ranges of Vs (Low, medium and high rates) also results in separate behaviors in terms of the development of color tonalities, in accordance with the fluence groups of [36].

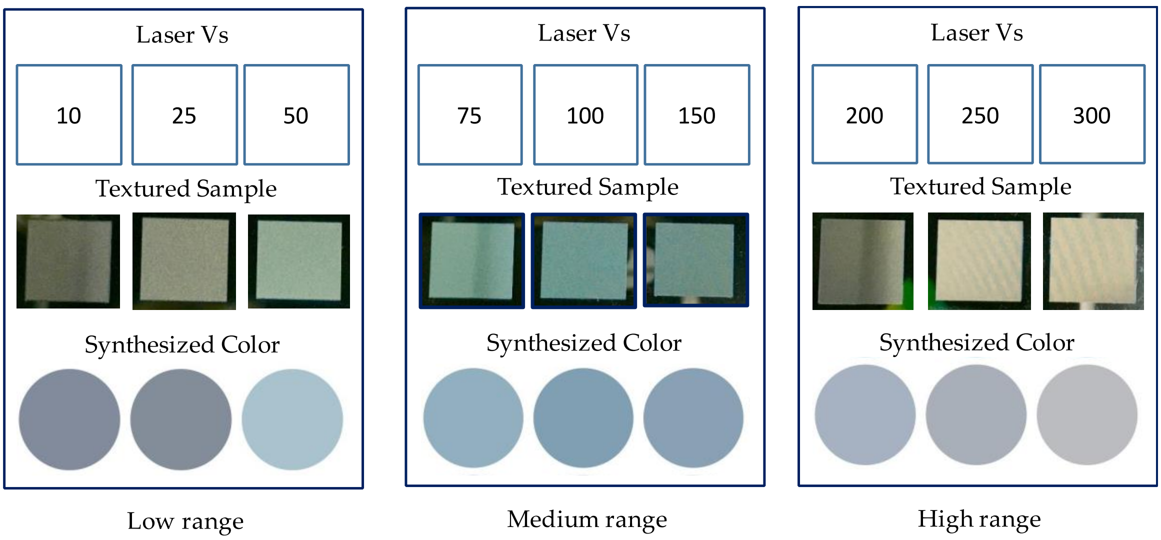


**Figure 7.** Color palette generate under different scanning speeds

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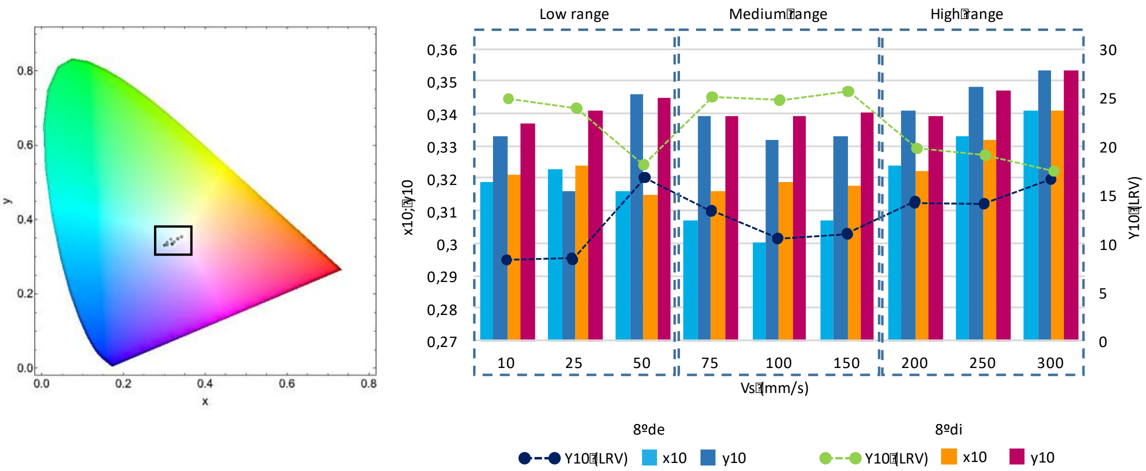
On these samples, the chromaticity coordinates Y10x10y10 were calculated from the reflectance spectra as measured with the integrating sphere and considering the standard colimetry observer CIE1964 and the illuminante D65. Values of the x10 and y10 color coordinates for the samples under study are shown in the CIE1931 chromaticity diagram, Fig. 8a.

The study of the different color coordinates shows reveals that the chromaticity coordinates (X10y10) are located in a small area on the center of the two dimensional diagram. This fact indicates a color locus quite reduced for this alloy and the parameters used in the study. However, through variations on the laser processing parameters, a wide variety in the color palette can be induced, according to [37].

The CIE 1931 color space (x10; y10 and Y10 (LRV)) indicates a singular point of the LRV value for 50 mm/s scanning speed of the beam. This feature can be observed on the synthesized color image of the lower Vs range, Fig. 7. Furthermore, a general growing trend was noticed for the color coordinate values (x10; y10) as a function of the Vs, Fig 8b. Likewise, most intense colors of the laser texturing conditions that were used in this research are located under higher values of Vs. However, there is a point of singular behavior for 50 mm/s, in connection with a change of trend in the shape of the laser tracks, mainly in terms of Rku. In addition, thanks to the micro-geometrical features of the textures under this processing conditions, an increase in the HAZ thickness was achieved, giving the best results to generate intense and lightness tonalities.




(a) (b)

**Figure 8.** (a) Color chromaticity diagram of the textures (b) Color coordinates behavior as a function of Vs

*3.5. Reflectance of the colored titanium surfaces*

Most of the researches about the reflectance of titanium alloys subjected to oxidative processes are focused on the development and analysis of continuous and flat surfaces. However, the possibility to incorporate additional properties by means of specific roughness topographies is shown as a gap in the study of this treatments. The sample color and reflectance shows an important dependency on the light incidence angle. This fact makes relevant the influence of the surface finish on the optical properties of the textured Ti6Al4V substrates.

The significant variation on the surface reflectance confirms the strong capability of the laser texturing processes for modifying the optical properties of metallic substrates. Wang et al. studies demonstrate that rough surfaces imply lower reflectivity values [28]. Under these considerations, may be confirmed that a decrease on the Vs led to a decrease in the absorption coefficient (α) of the surfaces. This fact indicates an attenuation of the reflectance properties as a function of the oxide layer thickness, obtained for lower scanning speeds.

Three main different groups of absorption coefficient behavior were also observed as in previous analysis of micro-geometrical and chromaticity properties, Fig. 9. Regarding to absorption coefficient, higher Vs values results in an increase of the reflectance of the textures. On the other hand, more aggressive treatments based on lower Vs generates surfaces with lower α values. The optical absorption phenomenon is in addition directly connected with the geometrical characteristics of the laser induced topography. The shape and depth of the laser grooves makes difficult the reflectance properties of the modified surfaces, resulting in low absorption coefficient values.

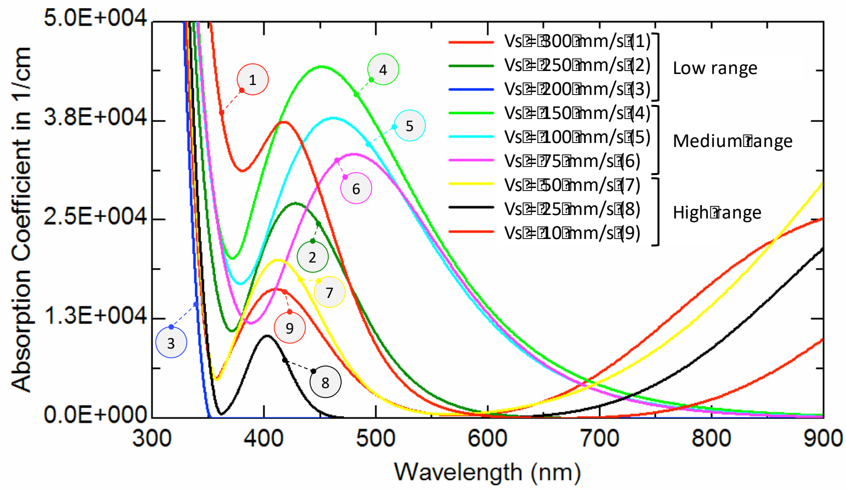



**Figure 9.** Absorption coefficient values of the laser textures

## 4. Conclusions

In this research, specific topographies combined with color surfaces of titanium have been obtained by changing the laser scanning speed in air atmosphere, using a fiber nanosecond pulsed laser. Experimental results confirm that the textured samples exhibit different roughness values combined with colorized surface, enhancing mechanical properties as hardness.

The development of the laser treatment under atmospheric environment contributes to the generation of an oxide film on the surface of the alloy. Mainly due to the rapid heating and cooling stages, associated with pulsed laser irradiation, these treatments also affect the Ti6Al4Vmicrostructure by transforming the closest areas of the laser tracks of the native surface to α′ martensite. A maximum area of higher than 4300 $\mu m^2$ on cross-sections of the textures, and track depth as large as 174 µm were measured for the lowest scanning speed experiments (10 mm/s).

Extreme temperatures focused on small spot diameter and cooling nature may affect the formation of the oxide film and the phase transformation close to the tracks. This may be the cause of the existence in isolated cases of crack growth over the texturing channels under most aggressive treatments (10 mm/s).

The existence of three scanning speed (Vs) ranges with clearly differentiated behaviors has been verified for all the evaluated parameters. Samples treated under lower range are characterized by deeper and narrow textured tracks with large thermal affected areas (HAZ) that induces important increases in hardness and lower absorption coefficient (α) values on near blue/grey color surfaces.

Chromaticity values are located in a small ellipse on the center of the CIE 1931 color coordinate diagram for all texturing conditions used in study. Main changes in optical properties of the textures were presented as increasing in the color coordinates (XYZ) and lightness (L*) as a function of the scanning speed of the beam. However, higher α values were detected in medium ranges of Vs. This suggest that the optically active film is strongly influenced by the deep and shape of the textures, in addition to the thickness of the HAZ.

This combined topography/color texturing method provides a new methodology for the development of multi-functional surfaces, expanding the application range of materials and increasing the performance of novel manufacturing processes.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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