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Surface modification of Ti6Al4V alloy by pulsed Yb-laser irradiation for enhanced adhesive bonding

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ABSTRACT

This work presents a comprehensive experimental study on the effect of pulsed laser ablation (Yb-fiber) on Ti6Al4V titanium alloy substrates for adhesive bonding. The modification of surface morphology and chemistry is assessed by means of SEM, XRD and wettability measurements. In addition, surface and subsurface mechanical properties are probed through an extensive series of instrumented indentation tests. Based on the results of the aforementioned analyses, a suitable processing window is identified and adhesive bonded T-peel joints are fabricated and tested. The obtained results indicate that pulsed laser irradiation can substantially improve the performance of Ti6Al4V/epoxy joints.

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1. Introduction

Q3 Titanium alloys are deployed in several applications, including medical and aerospace components. The good mechanical and physical properties, such as the high strength-to-weight ratio (up to 400–500 °C), make them very attractive in the design of lightweight aeronautical structures. However, the demand for reduced fuel consumption and increased payload capacity is forcing manufacturers to continuously optimize the overall aircrafts design. Therefore the replacement of traditional riveting with adhesive bonding is becoming more and more attractive. In this context, surface characteristics of the materials to be bonded play a crucial role. For instance, titanium sheets are fabricated by rolling processes, which affect bulk and surface properties [1]. It follows that titanium alloys need to be properly pretreated in order to achieve suitable surface conditions for reliable adhesive bonding. Chemical and/or electrochemical pre-treatments have been used for a very long time in the aeronautical industries. Chromic acid anodisation (CAA), phosphate–fluoride or sol–gel treatments, enable the modification of surface chemistry and morphology [2,3]. Though they provide fairly good bond strength and durability, major concerns arise because of the use and disposal of large volume of hazardous chemical waste, e.g. chromates compounds. As a result, there is a growing need to replace processes requiring the use of hazardous substances with environmentally friendly alternatives. Recent studies highlighted the great potential underlying the use of modern laser beams [4,5]. Laser irradiation can lead to the formation of a thin oxide layer featuring a nanostructured morphology and which actually resembles that obtained by means of chemical treatments [2,6–8]. However, there is still a paucity of contributions focused on the interaction between surface oxide and structural adhesives, and the resulting performance of adhesive bonded titanium alloys. This work aims to fill this gap and addresses the effect of laser irradiation on Ti6Al4V substrates. Surface conditions have been screened to draw quantitative information in terms of topography, chemistry and mechanical properties. In turn, the most suitable combination of laser processing parameters has been selected and adhesive bonded T-peel joints have been fabricated for subsequent mechanical testing.

2. Surface processing and characterization

The material used for the experimental campaign is a 1.5 mm thick Ti6Al4V sheet metal. Substrates have been cut out from the original work piece by cold blanking process. 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, roughness measurements, depth-sensing nanoindentation and X-ray diffraction (XRD). SEM and XRD analyses allow 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 treated surface to be properly wet by the liquid adhesive [5], while surface roughness can play a significant role on joint strength and therefore needs to be determined [9]. Finally, surface hardness of the treated material is assessed through nanoindentation tests, while the strength of Ti6Al4V/epoxy joints is analyzed using the T-peel test coupon.

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2.1. Laser treatment

After the blanking process samples were cleaned by means of ultrasonic bath in ethanol (99%) for 10 min at room temperature. Laser pre-treatment was subsequently performed by using a pulsed ytterbium doped fiber laser system (CL50 Clean-Lasersysteme, Germany) with 50 W maximum average power and 1062 nm wavelength. The pulsed laser beam had a pulse length (τ) of about 120 ns and was guided over the surface by a 2D scanning device. The beam was focused onto the surface by an F-theta lens (f = 160 mm) with a focus diameter of 25 μm. For the experimental campaign the scanning speed of the laser spot over the surface (v, mm/s), the pulse frequency (f, kHz) and, consequently, the pulse fluence (F, J/cm^2) were varied. As suggested in previous related work [4], laser power was kept constant to 5 W, while the line spacing (*i.e.* pitch) was set equal to 25 μm. In summary, F and v were varied over five levels as described in Table 1, giving raise to 25 laser processing combinations. Suitable laser treated samples were prepared for subsequent surface analysis and mechanical characterization.

Table 1
Experimental laser processing parameters.

Parameter	Value
Pulse fluence, F (J/cm^2)	10-20-30-40-50
Laser scanning speed, v (mm/s)	50-350-650-950-1250

2.2. Analysis of surface morphology and wettability

The SEM images of baseline (*i.e.* as received) and laser treated surfaces are displayed in Figs. 1 and 2. Laser irradiation enabled different extents of morphological modifications. At the lowest pulse fluence (10 J/cm^2), the treatment had little or no effect on surface topography.

This is exacerbated when the scanning speed is increased,

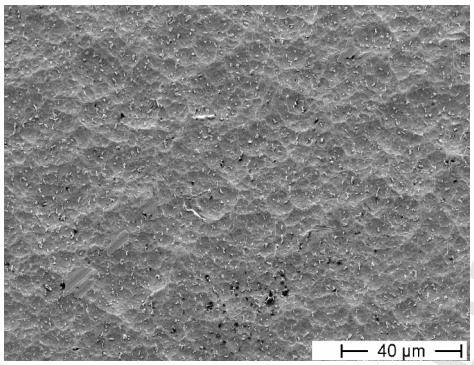


Fig. 1. SEM image of the as received Ti6Al4V alloy.

indeed laser irradiation closely resembled a cleaning process with rather limited modification of surface topography. For $F > 10$ J/cm^2 laser irradiation had a severe effect and induced extended surface melting, especially at the lowest scanning speed (*i.e.* v = 50 mm/s). For a given speed, a further increase in pulse fluence ($F > 20$ J/cm^2) did not lead to substantial modifications of surface topography.

Contact angle and surface roughness measurements were subsequently carried out. For the determination of contact angle, θ, the sessile drop technique was used (CAM 200, KSV Instruments Ltd., Finland). Bisphenol F diglycidyl ether liquid drops (3 μl) were placed on the titanium substrates to track the equilibrium contact angle as a function of the processing parameters. In order to screen all treated surfaces, and to ensure the robustness of the results, the average of five measurements was determined. The mean roughness, R_a, was determined by a non-contact profilometer provided with triangulation sensors (Vantage Cyberscan, Germany) able to deliver high-resolution (0.1 μm) height profiles. R_a was averaged over 10 measurements carried out with scan

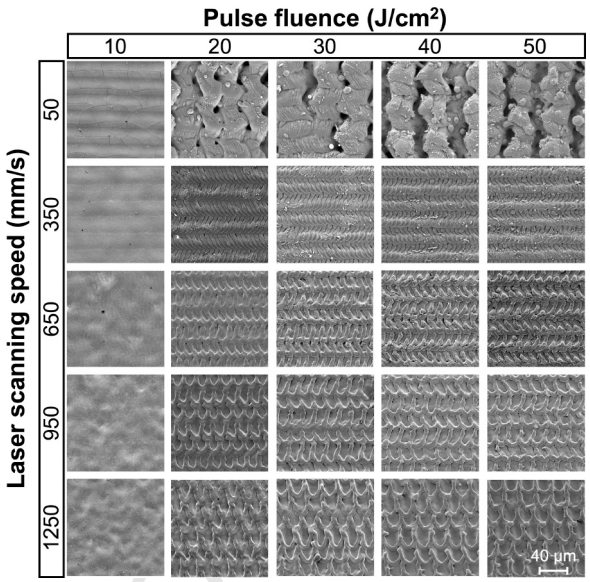


Fig. 2. SEM images of laser treated Ti6Al4V substrates as a function of laser scanning speed and pulse fluence.

gauge length equal to 25 mm. In particular, R_a was determined from the raw signal by filtering the spatial frequency content according to the DIN EN ISO 4288:1988. Fig. 3 summarizes the obtained values of contact angle θ and R_a.

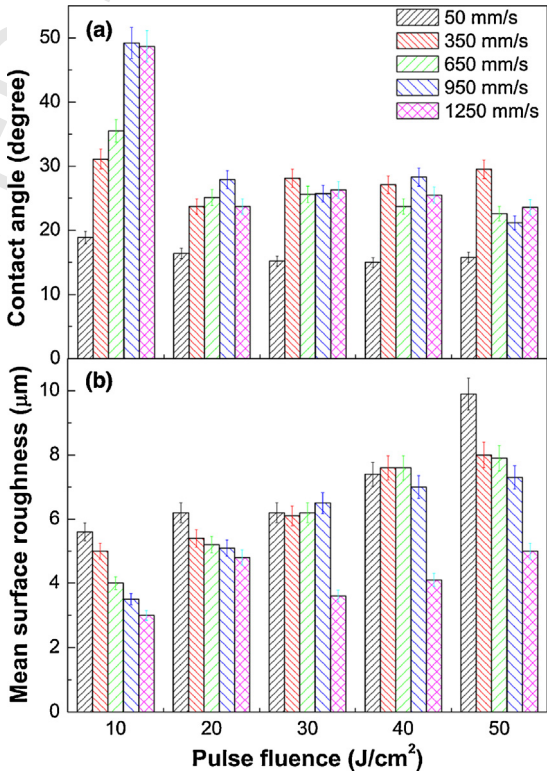


Fig. 3. Distributions of (a) contact angle and (b) mean roughness of laser treated Ti6Al4V substrates.

In particular, Fig. 3a displays the contact angle as a function of processing conditions; notice that the as received surface had $\theta \approx 60°$. The results show that θ consistently decreased by reducing the scanning speed, while a pulse fluence greater than 10 J/cm^2 had little or no effect on surface wetting. This might be a combined effect induced by modifications of surface topography and chemistry. Considering that the received surface had R_a = 2.4 μm, Fig. 3b shows that R_a was strongly modified by laser irradiation. In particular, R_a increased for increasing pulse fluence and decreasing scanning speed.

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The overall assessment of the obtained results suggests that increasing the pulse fluence and decreasing the scanning speed may offer the best tradeoff between wettability and surface roughness which, in turn, might enable mechanical interlocking.

2.3. Cross-sectional nanoindentation tests

Indentation tests were performed in the through-the-thickness direction by using a nanoindentation platform provided with a Berkovic tip (NH^2 CSM Nanoindentation Platform). The samples were cold mounted in epoxy resin over the cross section and then gently polished. Preliminary tests were carried out to properly select suitable values of maximum load and dwell time. As suggested in [10,11], maximum loads ranging from 5 to 500 mN and dwell times from 5 to 187 s were preliminary screened, and subsequently they were set equal to 50 mN and 10 s, respectively. Indentations were performed from the top surface in the through-thickness direction. The spacing between each indent was about four times the imprint diagonal to prevent the mutual influence of consecutive indentations. Fig. 4 shows the distribution of indentation hardness, *HIT*, for selected processing conditions.

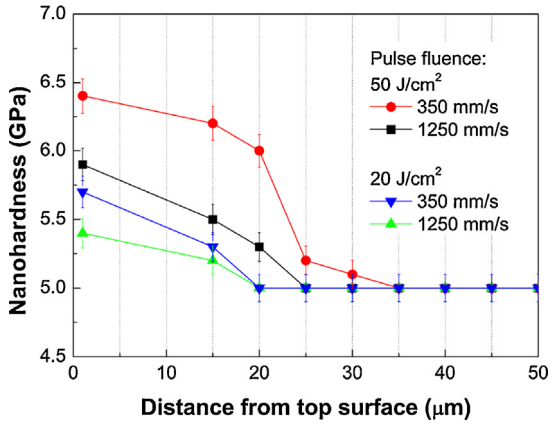


Fig. 4. Distribution of nanoindentation hardness for selected laser treated Ti6Al4V substrates.

The results, which were averaged over five consecutive measurements, indicate that laser irradiation enhanced surface hardness with respect to the bulk material (*i.e.* 5 GPa). However, the extent of the resulting modification and the through-thickness profile of *HIT* depended on pulse fluence and scanning speed. Samples treated at the lowest pulse fluence (not reported herein) displayed negligible hardness modifications, while for $F \geq 20$ J/cm^2 *HIT* always increased (see Fig. 4). In particular, the highest hardness generally occurred at the top surface and increased for increasing pulse fluence and decreasing scanning speed.

Notice that an increase in pulse fluence generates transient pools of molten material on the target surface (see Fig. 2). Owing to the fast heat dissipation through the cooler surrounding material, substrate melting is followed by fast self-quenching and the formation of a rapidly solidified hard layer [12–14]. By decreasing the scanning speed, the interaction time between the laser beam and the target surface is extended. As a result, the average energy deposited by the laser spot, as well as the maximum temperature on the target surface, increased. Therefore, at low scanning speed surface melting and rapid self-quenching were further promoted thereby sustaining the formation of harder compounds. This is also testified by the results obtained at $v = 50$ mm/s which displayed the highest surface hardness recorded in our tests (see Fig. 5). However, the so obtained top surface oxide layer is weakened by the presence of micron-sized voids likely associated to air bubbles trapped during solidification [15,16].

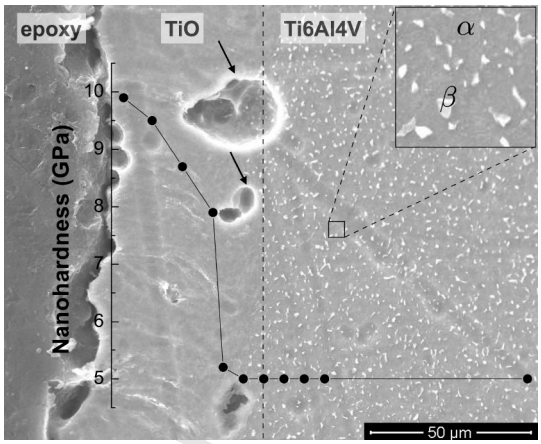


Fig. 5. Cross sectional SEM image of laser treated sample at $v = 50$ mm/s and $F = 50$ J/cm^2. The *HIT* profile is also superimposed. The arrows indicate large voids generated by the laser process.

2.4. X-ray diffraction analysis

X-ray diffraction patterns are reported in Fig. 6. The XRD spectrum of as received surface testifies the presence of α-Ti [JCPDS file #44-1294] and β-Ti [JCPDS file #44-1288] phases, which are also shown in the insert of Fig. 5. Material melting that follows laser irradiation determined surface recrystallization and a broadening of the α peaks [17].

This phenomenon is explained with the formation of α'-phase (*i.e.* supersaturated martensitic phase with hexagonal close-packed structure) that is promoted by the high surface temperature and the subsequent fast cooling rate [2,12–14]. Thus, the observed increase of *HIT* at high pulse fluence and low scanning speed is associated to the formation of α' martensite. Finally, it is worth noting that samples processed at 50 mm/s and 50 J/cm^2 displayed two additional XRD peaks which are attributed to the formation of TiO [JCPDS file #23-1078] [17]. The formation of a TiO oxide layer was confirmed by the violet to green color shown by the surface after the treatment [15].

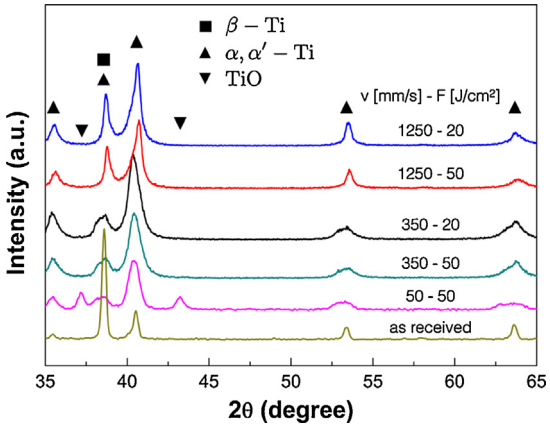


Fig. 6. XRD patterns of the Ti6Al4V alloy as a function of scanning speed and pulse fluence.

3. Fabrication and testing of T-peel Ti6Al4V/epoxy joints

Four combinations of laser processing parameters were selected for samples fabrication. Specifically, two levels of scanning speed (350 and 1250 mm/s) and pulse fluence (20 and 50 J/cm^2) were considered. The choice was supported by the following observations. The laser treatments performed at $F = 10$ J/cm^2 did not provide significant surface modifications. In addition, irradiations made at the lowest scanning speed ($v = 50$ mm/s) led to the formation of a weak oxide layer affected by the presence of micron-sized voids. Moreover, the hardness profile indicated an

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abrupt variation from top surface to bulk material with no gradual transition (see Fig. 5). These observations suggest that the resulting oxide layer might be easily detached from the substrate and could affect the overall mechanical response of T-peel joints. The issue associated to surface induced damage following laser irradiation was also discussed in a recent related work [18].

Titanium substrates were cut down to 15 mm × 100 mm substrates. Laser treatment was performed over an area 15 mm × 60 mm while the remaining portion was bent to achieve the desired L-shape (see Fig. 7). Surface preparation of as received samples was carried out using solvent degreasing. A two-component toughened epoxy adhesive (Loctite EA 9466, Germany) was deployed and the bondline thickness was set equal to 0.2 mm by means of spacers. Five T-peel samples for each testing condition were fabricated. After curing at room temperature for 48 h, tensile tests we carried out using an electromechanical testing machine (MTS Criterion 42 Series). The displacement rate was set equal to 1 mm/min.

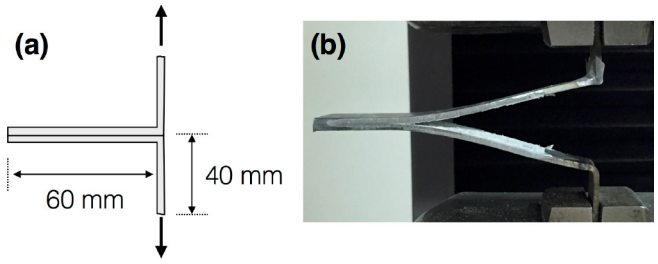


Fig. 7. (a) Schematic of the T-peel test geometry and (b) picture of the actual sample taken during mechanical tests.

In T-peel tests the bondline is subjected to peel loading and joints failure involves crack propagation. This feature is useful because the total dissipated energy (*i.e.* area under the load–displacement response) per bonded area can be used to screen the effect of laser treatments [19]. The total absorbed energy, which is given in Fig. 8, testifies the beneficial effect of laser irradiation. Indeed, compared to as received samples, a several fold increase was recorded (50×).

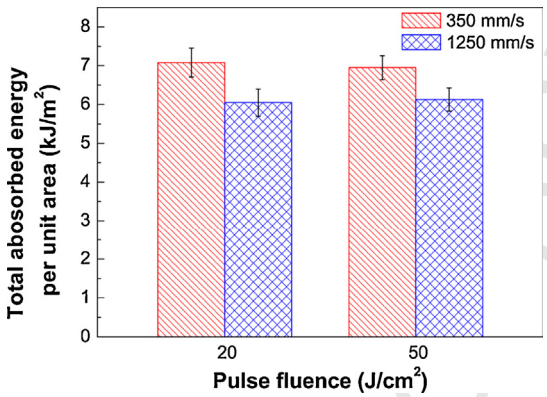


Fig. 8. Total absorbed energy recorded in T-peel tests carried out on Ti6Al4V/epoxy joints. Notice that the total absorbed energy per unit area recorded on as received samples was equal to ≈0.15 kJ/m².

The data given in Fig. 8 allow to conclude that the total energy dissipated was mostly sensitive to scanning speed rather than pulse fluence. This result nicely matches with SEM analyses which indicated that the most significant surface morphological modifications were generated by varying the scanning speed. Finally, visual inspection of the fracture surfaces have shown near interfacial failure for the as received samples and full cohesive (within the adhesive layer) failure for the laser treated samples. These findings also confirm that the chosen combinations of processing parameters were able to enhance contact area and promoted mechanical interlocking.

4. Conclusions

The present work addressed the effect of pulsed laser pre-treatment on Ti6Al4V surfaces for enhanced adhesive bonding. Laser irradiation generated substantial modifications of surface topography and chemistry and was able to increase mean roughness, wettability and surface hardness. The total dissipated energy, measured in T-peel tests carried out on Ti6Al4V/epoxy joints, was several folds higher than that achieved with as received substrates. Therefore, laser irradiation was proven to be a very effective surface preparation technique able to enhance the peel resistance of adhesive bonded titanium alloys.

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