

Article

Raman Spectroscopy of Laser-Micro-Annealing-Induced Structural Changes in Ti-6Al-4V

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Abstract

This short study presents the results of micro-Raman investigations performed on the alloy Ti-6Al-4V, which was additively manufactured via metal fused filament fabrication (MF³). Local laser micro-annealing was applied at different power intensities to distinct regions. The applied laser power density was varied in the range of ~0.05 kW/cm² to ~5 MW/cm². Laser-induced compositional changes in structures, approx. 1 µm in diameter, arranged in an array, are laterally limited. Simultaneously, the surrounding matrix maintains its initial pristine material properties down to ~500 nm in spacing between neighboring structures, reproducibly. The presented results confirmed that the material contains residues of the organic-based binder system and its decomposition products. Besides the characteristic Raman modes related to hydrocarbon compounds, TiC, and defect carbon phases were identified. Unexpectedly, micro-Raman mapping measurements performed on regions exposed to laser power densities above 2.5 MW/cm² for up to 2 min revealed the complete suppression of hydrocarbon modes. Additionally, laser micro-annealing applied under identical operating conditions initiates “carbonization” processes in regions predominantly composed of residues from the organic-based binder used in material preparation. This short initialization study is a prerequisite and first building block for the development of suitable laser annealing technology which allows the modification and functional texturization of Ti-6Al-4V alloys down to the sub-micro scale. The correlation between modified materials’ structural and mechanical properties will be the aim of our future studies. This would allow the design and fabrication of sophisticated tools using MF³ technology for, e.g., surgery biocompatible implants with locally tuned, favorable mechanical properties.



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1. Introduction

The next generation of micrometer-sized devices for special applications and harsh environments, such as those used in space research and exploration, requires fabrication tools and technologies that can simultaneously transport materials, develop heat locally in

microscale regions, and facilitate chemical reactions in the target area. Therefore, alternative device fabrication technology that implements different conventional tools and techniques within a hybrid multichannel injector architecture could significantly improve the material properties locally at the micrometer scale. The small dimensions of regions that can be functionally designed with respect to the tuning of their mechanical properties would be advantageous and would allow for the realization of, e.g., complex material textures with locally tuned mechanical properties. Hence, it can be expected that such novel material systems/architectures would exhibit physical, chemical, mechanical, optical, and electrical properties that differ strongly from materials fabricated using established, e.g., metal injection/printing, laser-assisted “melting”, and/or annealing techniques [1–11]. Researchers also paid special attention to post-processing of additively manufactured titanium alloys [12–17]. Future trends in this technological field would certainly benefit from the enormous number of fabrication techniques developed over the last 50 years, especially those employing lasers as energy sources [18–21]. It is well known that laser annealing can be used for repairing ion- and/or radiation-induced damage [22–25], as well as for processing micro- and nanostructures, particularly for annealing contacts to nanostructures [25–30]. The latter studies generally aimed to reduce contact resistance and, for practical and industrial applications, to use the shortest possible annealing times. In contrast, our study focuses on structural processes and their evolution on the microscale that are initiated during the longer (up to several minutes) time scale of laser exposure. Monitoring of such structural and/or phase changes, local strain distribution, and the development and/or transformation of chemical compounds can be performed using the Raman spectroscopy technique [30–37].

Our work represents the first building block necessary for the realization/developing of a large-array multi-injector “head” solution [38] for material texturization down to the micrometer and, prospectively, to the sub-micrometer scale required for advanced 3D printing technologies. Nevertheless, the impact of material modification by laser exposure in such small dimensions, revealed by micro-Raman spectroscopy, as presented in this short study, represents a first important step to establish a correlation with the mechanical properties (which will be the target of our future investigations). Characterizing the impurities in the Ti-6Al-4V specimens using micro-Raman spectroscopy helps us understand the effect of laser micro-annealing on extrinsic impurities resulting from the technological processes used to prepare them. These impurities are unexpected residues or products of the organic binder system that were not fully removed during extensive thermal decomposition or pyrolysis processes. They affect the mechanical properties in various ways [39–41]. The investigation of the mechanical properties of materials modified by laser-micro-annealing, however, will be the scope of a separate comprehensive study on a series of materials with different binder compositions and optimized debinding treatments. In Section 3, we present a “proof of principle” laser annealing procedure that induces local structural changes in lateral dimensions of about 1 μm in diameter while simultaneously preserving the initial pristine material properties of the regions between neighboring structures (allowing to achieve minimum technologically possible spacing), reproducibly. The experimental results are presented on samples fabricated from a representative material system described in Section 2.

2. Materials and Methods

A commercial Ti-6Al-4V powder (Grade 23, Tekna Advanced Materials Inc., Sherbrooke, QC, Canada) with a density of 4.4 g/cm³, an average particle size (d_{50}) of 28.6 μm , and a specific surface area of 0.15 m²/g was used. The carbon and oxygen contents were 0.008 wt.% and 0.09 wt.%, respectively. The organic binder was composed of poly(vinyl

butyral) (PVB, Mowital 30H, Kuraray Europe GmbH, Frankfurt, Germany), polyethylene glycol (PEG 8000, C. Roth GmbH Co. KG, Karlsruhe, Germany) and acetyl tributyl citrate (ATBC, Sigma Aldrich, St. Louis, MO, USA). The solid load of the feedstock was set to 60 vol.%. Information on the development and the properties of the binder system can be found in [42,43]. The samples were debound using a three-step process. First, PEG was extracted in a water bath at 30 °C. Subsequently, ATBC was removed in a thermal pre-debinding process under an oxygen atmosphere at 230 °C. Finally, thermal debinding was performed to pyrolyze the remaining binder components using a heating rate of 1.5 °C min⁻¹ up to a maximum temperature of 550 °C. The debound specimens were then sintered in a metal sintering furnace (MUT Advanced Heating GmbH, Jena, Germany) at a heating rate of 5 °C min⁻¹ and a maximum temperature of 1350 °C. Both thermal debinding and sintering were conducted under an argon atmosphere to minimize oxygen and nitrogen contamination.

The Raman studies were carried out on the sintered samples in a confocal Raman microscope (Renishaw inVia FSM REFLEX, New Mills, Gloucestershire, UK) in backscattering geometry, which was equipped with a frequency-doubled Nd-YAG laser (532 nm, 50 mW) and a CCD detector. The backscattered signal was collected through a 100× objective lens (Leica, NA 0.85, (Product Nr. 566073, Contrasting Methods 456TL/05), Wetzlar, Germany) and dispersed by a grating with 2400 grooves per mm. According to the technical specifications provided by Renishaw plc (www.renishaw.com), the laser beam has a spot diameter of ~1 µm and the spectral resolution is 1 cm⁻¹. The spectrometer was referenced to the transverse optical phonon of Si at 521 cm⁻¹. Spectra were recorded in the range between 100 cm⁻¹ and 2000 cm⁻¹. An average optical power density of ~0.05 kW/cm² used for our Raman spectroscopy investigations was reproducibly identified as a power density that does not initiate any surface morphology or structural changes in pristine regions of the Ti-6Al-4V specimens. This laser power density level was estimated according to our previous experimental procedures reported, to stay below the material's thermal damage threshold [44–46]. Six Raman spectra were collected at each distinct position for the sake of statistics. A careful comparison of groups of six spectra revealed that they were almost identical. Therefore, we decided to present one representative Raman spectrum from the six measured.

After the characterization of the pristine specimens at selected representative morphological areas, local laser micro-annealing was carried out using a frequency-doubled Nd-YAG laser (532 nm, 50 mW, Renishaw, New Mills, Gloucestershire, UK) in the average laser power density range of approximately 0.05 kW/cm² to 5 MW/cm² for one min. The average laser power density is the total power incident on the entire sample area [47]. The beam area is calculated from the 1/e²-diameter of the Gaussian beam profile. The power density was calibrated at room temperature using a spectrophotometer (Agilent Cary 5000, Santa Clara, CA, USA).

3. Results and Discussion

The optical micrograph presented in Figure 1a shows a typical surface morphology of regions in which the metallic character has fully developed into Ti-6Al-4V “islands” after thermal annealing (following debinding at 550 °C and sintering at 1350 °C). These “islands” are surrounded by the residues and/or products of binder decomposition reactions. Their presence was confirmed through optical inspection as well as through the measured representative Raman spectra in Figure 2 shown later. As mentioned in Section 2, an organic mixture of PVB, PEG and ATBC was used as a binder for preparing the materials (MF³ technology). It should be noted that the unexpected recognition/presence of signatures of residual organic binder educts/products after a sintering process performed at 1350 °C

cannot currently be fully explained. Nevertheless, we assume that the presence of complex organic molecules in material systems/objects exposed to extremely high temperatures, such as in meteorites, could at least provide evidence that such effects cannot be ruled out in general. In particular, complex organic decomposition compounds entrapped in the Murchison meteorite, for example, have been reported [48,49], even though the meteorite could reach temperatures above 2000 °C upon atmospheric reentry [50,51]. Similarly, this may indicate that a sintering temperature of 1350 °C, as in our case, is, under certain material-technological conditions, insufficient to completely remove all reaction products and by-products (i.e., the binder materials PVB, PEG and ATBC and their decomposition reaction products), which may become entrapped in the final product—our investigated Ti-6Al-4V metal alloy specimens. However, extensive research is required to reveal this unexpected phenomenon, and the chemical and physical mechanisms behind such effects will certainly be studied in more detail in the future.

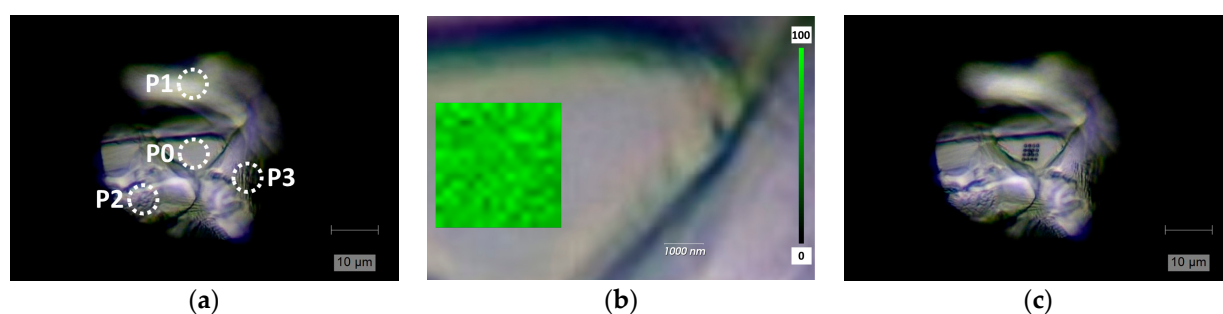


Figure 1. (a) Optical micrograph of the Ti-6Al-4V alloy before laser exposure and (b) micro-Raman mapping intensity image for the Raman mode 800 cm^{-1} (corresponding to hydrocarbons) performed on the region P0, demonstrating an almost uniform distribution, and (c) after the laser micro-annealing procedure was performed/applied in 16 positions. It should be noted that this is only one representative example of arrays which were used for this study.

In the following, we characterized the regions P0, P1, P2 and P3 presented in Figure 1a using micro-Raman measurements before a laser micro-annealing procedure was performed (on, e.g., 16 positions; see Figure 1c). A representative Raman spectrum presented in Figure 2a, collected in the central metallic/clean region before laser exposure (corresponding to position P0 in Figure 1a), reveals only weak, broad Raman modes at $\sim 800\text{ cm}^{-1}$ assigned to rather unspecific C–C skeletal/conformational modes in polymers [32] and a mode at $\sim 440\text{ cm}^{-1}$. The micro-Raman mapping image presented in Figure 1b reveals a nearly uniform intensity distribution of the 800 cm^{-1} Raman mode in the P0 region. The micro-Raman measurements were performed before the laser micro-annealing experiments. A micrograph of this area after laser micro-annealing is presented in Figure 1c. In contrast, the top region (position P1—identical in Figure 1a,c) represents the typical morphology, where the residue of binder products surrounds regions that are almost “metallic”. After inspecting large areas of the investigated Ti-6Al-4V material, we can conclude that the Raman mode at $\sim 800\text{ cm}^{-1}$ (assigned to C–C skeletal/conformational modes) is distributed inhomogeneously on the microscopic scale. Several dominant narrow modes in the range between 1000 and 2000 cm^{-1} are visible in the Raman spectrum presented in Figure 2b. These skeletal conformational C–C Raman modes are induced by backbone vibrations related to differences in chain conformation, crystallinity, orientation, and disorder in the organic binder-related products and their decomposition reaction products [32,52,53]. As mentioned above, the unexpected presence of organic products related to the binder and its decomposition reaction products in Ti-6Al-4V specimens after the sintering process cannot be clarified in this short study. However, consistent material properties resulting

from technological advances could lead to the design of new metal/alloy-organic compound composite materials with adjustable properties. For instance, these materials could have enhanced mechanical parameters and/or radiation hardness, making them ideal for use in harsh environments, such as those encountered in space research or nuclear/fusion applications. This should, of course, be clarified and confirmed by future studies. Progress in revealing the mechanism and identifying the organic compounds present in meteorites will undoubtedly inspire further research into this phenomenon [48,49].

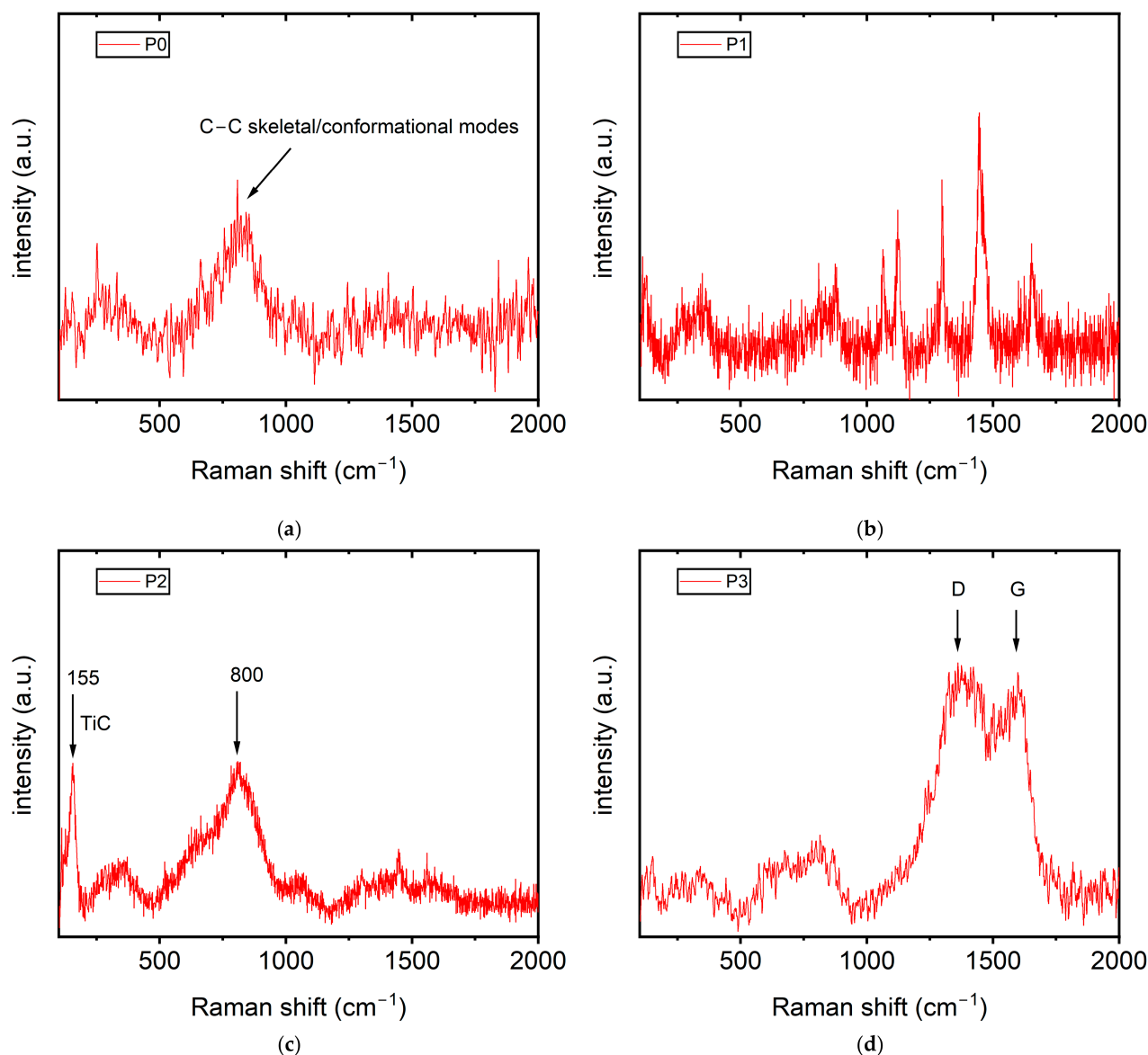


Figure 2. Representative Raman spectra collected in the (a) metallic/clean region, prior to laser exposure (P0 in Figure 1a) and the (b) “binder-residue” region (P1 in Figure 1a). The Raman band at $\sim 800\text{ cm}^{-1}$ is assigned to C–C skeletal/conformational modes, while the modes above 1000 cm^{-1} are fingerprints of residual binder-related adducts and their decomposition reaction products. Spectrum (c) (P2 in Figure 1a) reveals characteristic TiC-related Raman modes. Spectrum (d) (P3 in Figure 1a) exhibits the carbon D ($\sim 1360\text{ cm}^{-1}$) and G ($\sim 1590\text{ cm}^{-1}$) bands, respectively. The laser beam was focused on the surface through a $100\times$ (NA 0.85) objective lens. The average optical power density was $\sim 0.05\text{ kW/cm}^2$. The acquisition time was set to 10 s. The total acquisition time (measurement duration) is defined as the sum of acquisition time, data processing, movement of mechanical components, etc., and takes 50 s for every single measured spectrum (from 100 cm^{-1} to 2000 cm^{-1}).

A representative Raman spectrum shown in Figure 2c, collected at position P2 (left side of Figure 1a), revealed a strong increase in the Raman mode at around 155 cm^{-1} , indicating the local presence of TiC [54,55]. Even though first-order Raman scattering is forbidden for stoichiometric TiC [56–58], broad bands induced by carbon-vacancy disorder can be observed at $\sim 260\text{ cm}^{-1}$, $\sim 440\text{ cm}^{-1}$, and $\sim 605\text{ cm}^{-1}$ [56,59] for non-stoichiometric material due to the loss of the inversion center in the material observed. In addition, residual carbon is present, as evidenced by the appearance of D and G Raman bands that are slightly shifted from their characteristic positions [60]. Conversely, measurements performed in the right region (position P3, Figure 2d) of Figure 1a confirmed the presence of broad Raman modes at $\sim 1360\text{ cm}^{-1}$ and $\sim 1590\text{ cm}^{-1}$ [61,62], which are assigned to carbon D and G modes, respectively. Their intensities and full width at half maximum (FWHM) indicate the presence of defective carbon phases [61,62].

For comparison, micro-Raman mapping measurements were also performed on all fabricated samples with an area of approximately $10\text{ mm} \times 10\text{ mm}$ (Ti-6Al-4V specimen). The results confirmed the presence of carbon-related modes and their inhomogeneous distribution, as exemplified in Figure 3. Unfortunately, the inhomogeneous nature of the samples made it more difficult to demonstrate the major goal, i.e., proof of principle, of this short study: “the laser annealing procedure induces local structural changes within lateral dimensions of approximately $1\text{ }\mu\text{m}$ while simultaneously preserving the pristine material properties in the space (area) between neighboring structures”. The minimum distance (spacing) between neighboring structures that can be achieved can be experimentally estimated.

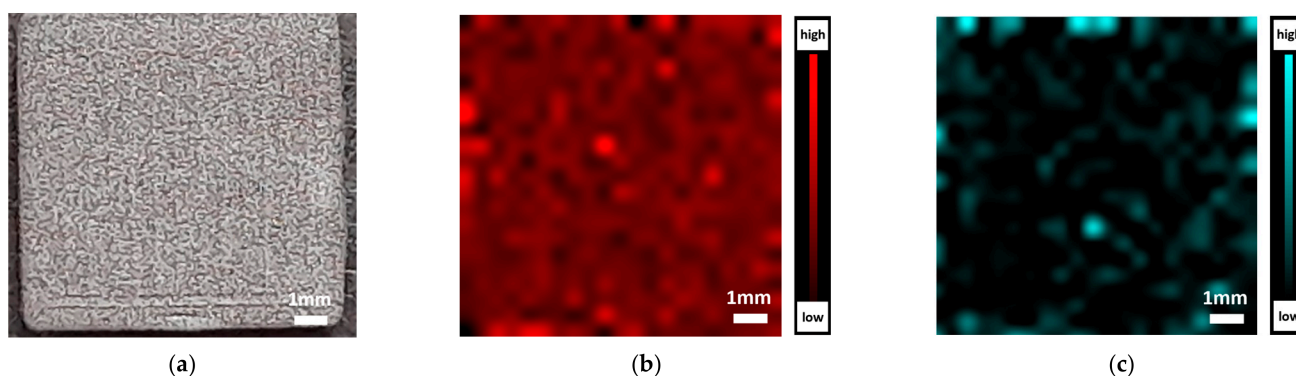


Figure 3. (a) Optical micrograph of the Ti-6Al-4V material/specimen with a size of approx. $10\text{ mm} \times 10\text{ mm}$. Micro-Raman intensity mappings performed at (b) 1360 cm^{-1} and (c) 1590 cm^{-1} showing that carbon-related compounds are distributed inhomogeneously on the macroscopic scale. A $5\times$ Leica objective (NA 0.12) collected the backscattered signal, which was then dispersed using a grating with 2400 grooves per millimeter. The average optical power density was $\sim 0.05\text{ kW/cm}^2$. The mapping step size was $50\text{ }\mu\text{m}$, and the laser spot size was $70\text{ }\mu\text{m}$. To achieve a $70\text{ }\mu\text{m}$ defocused laser beam on a Renishaw Raman InVia microscope using a $5\times$ Leica (NA 0.12) objective lens, the precise z-axis offset was calculated and set by the WiRE 5 software (Renishaw plc, New Mills, Gloucestershire, UK). The Raman mapping measurements were performed in static mode, and the acquisition time was set to one second (per measurement position on the sample). The total measurement time (duration) was approximately 12 h. It should be noted here that the area of the presented micro-Raman intensity mapping images is slightly smaller than $10\text{ mm} \times 10\text{ mm}$. This is to eliminate the possible effects of the specimen’s sidewall and the interaction/contribution of the sample holder during measurements.

Before the laser micro-annealing procedure was applied, we first identified areas of the sample with nearly identical material properties, as was already shown in Figure 1b (region

P0). Here, it should be noted that such areas/regions were identified by micro-Raman mapping measurements on all samples before laser micro-annealing was applied.

Figure 4 presents one example of the results of micro-Raman mapping measurements performed on a representative array containing 16 laser-treated positions. Prior to laser micro-annealing, the entire area was characterized by micro-Raman mapping. These measurements revealed a nearly uniform distribution of a weak, broad Raman mode at 800 cm^{-1} , which is assigned to rather unspecific C–C skeletal/conformational modes in polymers [32]. A representative Raman spectrum in this region is displayed in Figure 2a (position P0) of Figure 1a. Intensity mapping of the measured Raman modes at 155 cm^{-1} (Figure 4a), 440 cm^{-1} (Figure 4b) and 605 cm^{-1} (Figure 4c) confirms the local transformation (down to $1\text{ }\mu\text{m}$ in diameter) of the laser-annealed/exposed areas and reveals a strong decrease in intensity in the center of the laser-annealed regions/positions. On the other hand, an almost uniform distribution of the 800 cm^{-1} Raman mode is observed in the non-laser-annealed/exposed areas (Figure 4d). This result demonstrates the presence of hydrocarbons with characteristic Raman modes in the outer original matrix surrounding laser-annealed/exposed areas, as well as especially between neighboring structures with spacing down to 500 nm , as revealed by careful inspection of micro-Raman mapping data. The latter result is in very good agreement with our initial micro-Raman mapping measurements on the targeted region before laser-micro-annealing was applied, which exhibited uniform intensity of the 800 cm^{-1} mode. It should be noted that the laser-micro-annealing process performed in this study is highly reproducible, and the data collected for all four micro-Raman mappings presented in Figure 4 originate from the area shown in Figure 1b. This is only one representative example; we repeated these kinds of investigations six times for statistical evaluation.

Figure 5 shows representative Raman spectra collected in the middle of the area that had been exposed to a continuous wave (cw) laser for an average optical power density ranging from $\sim 0.05\text{ kW/cm}^2$ to $\sim 5\text{ MW/cm}^2$ over a period of one minute. At $\sim 0.05\text{ kW/cm}^2$, the spectrum is dominated by the $\sim 800\text{ cm}^{-1}$ mode associated with hydrocarbons (C–C skeletal/conformational modes). Furthermore, the results confirm that Ti-6Al-4V can withstand laser exposure with average power densities ranging from $\sim 0.05\text{ kW/cm}^2$ to $\sim 5\text{ kW/cm}^2$ for one minute without significant changes occurring that can be detected by Raman measurements. The intensity of the $\sim 800\text{ cm}^{-1}$ mode becomes less dominant as the average laser power (annealing) density increases further until suppression (a decrease in the measured intensity) is observed in the range of $\sim 2.5\text{ MW/cm}^2$ to $\sim 5\text{ MW/cm}^2$. Conversely, at $\sim 50\text{ kW}/\mu\text{m}^2$, characteristic Raman modes at $\sim 155\text{ cm}^{-1}$, $\sim 440\text{ cm}^{-1}$ and $\sim 605\text{ cm}^{-1}$, associated with TiC, start to evolve and become more intense up to $\sim 2.5\text{ MW/cm}^2$, proving that substantial localized structural and chemical changes have been initiated by laser-micro-annealing, most probably leading to the reaction of hydrocarbons with Ti and to the formation of TiC.

Representative Raman spectra for one and two minutes of laser exposure time with an average laser power density of $\sim 2.5\text{ MW/cm}^2$ were collected at coordinates $[x = 3, y = 2]$, which are identical to the layout of the laser-exposed regions in Figure 4. They are presented in Figure 6. However, increasing the laser annealing time from one (Figure 6a) to two minutes resulted in structural and chemical changes in the central exposure regions, as can be seen in the Raman spectrum presented in Figure 6b. The Raman mode at $\sim 800\text{ cm}^{-1}$ (assigned to C–C skeletal/conformational modes) has been almost completely suppressed. This indicates that, in addition to the average laser power density increasing from $\sim 2.5\text{ MW/cm}^2$ to $\sim 5\text{ MW/cm}^2$, an increase in local laser annealing exposure time also reduces the hydrocarbon content in the exposed area.

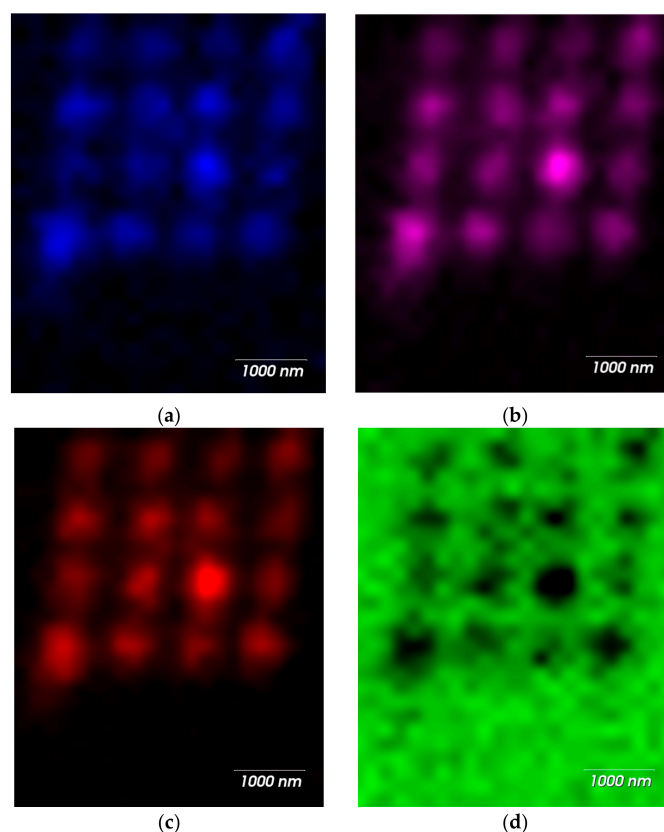


Figure 4. Examples of selected Raman intensity images generated (by WiRE software, Renishaw plc.) from the data collected by micro-Raman mapping measurements performed (from 100 cm^{-1} to 2000 cm^{-1}) on a representative array, where the laser-micro-annealing procedure was carried out/applied at 16 positions (see Figure 1c). The laser beam was focused on the surface through a $100\times$ (NA 0.85) objective lens. The average optical power density was $\sim 0.05\text{ kW/cm}^2$. The acquisition time was set to 10 s. The mapping step size was 200 nm. The total acquisition time (measurement duration) was $\sim 7\text{ h}$. Micro-Raman intensity mapping images are displayed (four characteristic peaks) as follows: (a) 155 cm^{-1} , (b) 440 cm^{-1} , (c) 605 cm^{-1} associated with TiC, and (d) 800 cm^{-1} associated with C–C skeletal/conformational modes. The Raman intensity data presented in the images (for all displayed Raman modes) are color-coded as follows: black indicates zero intensity, while the highest intensity is attributed to the most intense shades of blue, magenta, red, and green. While the intensity of the hydrocarbon compounds decreases upon local micro-laser annealing, the intensity of the modes associated with TiC increases.

As shown in Figure 7, the laser-micro-annealing procedure was also applied to the region of the specimen investigated where residues of the binder polymer mixture were predominantly identified. Figure 2b already shows a representative Raman spectrum exhibiting narrow modes in the range between 1000 and 2000 cm^{-1} . Comparing that spectrum, which was collected in the non-laser-annealed exposure region, with representative Raman spectra collected in the “binder residue” region exposed to average optical power densities ranging from $\sim 250\text{ kW/cm}^2$ to $\sim 500\text{ kW/cm}^2$ for one minute (exposure time), no significant changes in the recorded Raman spectra were revealed. However, dramatic changes in the “Raman signature” were detected in these laser exposure regions for average laser power densities of $\sim 2.5\text{ MW/cm}^2$ and $\sim 5\text{ MW/cm}^2$. While the visible maxima of the presented Raman modes (at these two high average laser power densities) are not precisely located at the well-known characteristic Raman modes (D and G) for carbon-related compounds, we can conclude that, thermal effects lead to a “carbonization” process in the targeted region between $\sim 500\text{ kW/cm}^2$ and $\sim 2.5\text{ MW/cm}^2$ and cause the characteristic Raman modes related to binder polymer-mixture residues to disappear. Further investiga-

tions are planned and will be included in our comprehensive study to be submitted in the future. Nevertheless, these results suggest that the careful tuning of process parameters, such as exposure power and time during laser micro-annealing, can substantially change both the “metallic character” and “binder-polymer residue” regions when applied locally. These processes can lead to the local modification of Ti-6Al-4V containing organic-based binder products, with the prospective aim of tuning their mechanical properties. This would also enable surface texturization and localized functionalization of materials down to the micrometer scale.

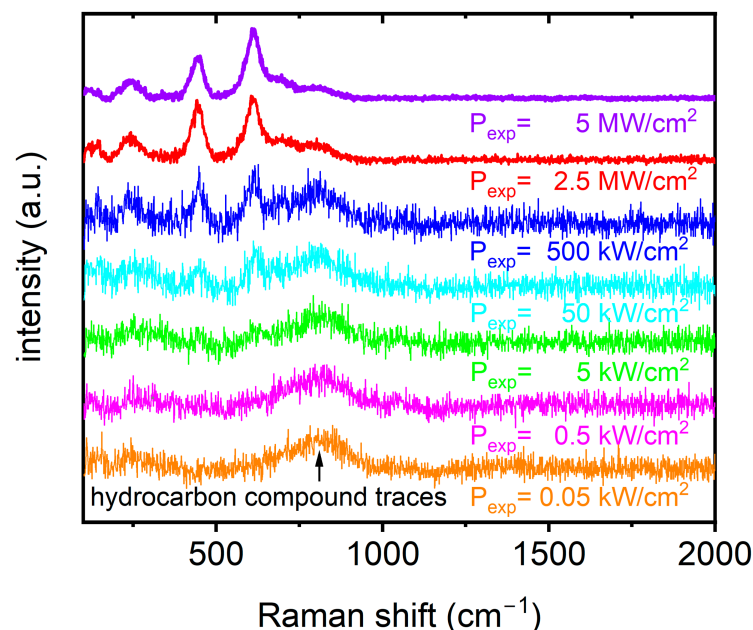


Figure 5. Representative Raman spectra collected in the middle of the cw laser-exposed area for average optical power densities ranging from $\sim 0.05 \text{ kW/cm}^2$ to $\sim 5 \text{ MW/cm}^2$ for one minute exposure. The laser beam was focused on the surface through a $100\times$ (NA 0.85) objective lens. The acquisition time was set to 10 s. As the average optical power density increases, the intensity of modes related to TiC increases. At $\sim 2.5 \text{ MW/cm}^2$ and $\sim 5 \text{ MW/cm}^2$, the mode related to hydrocarbons is suppressed.

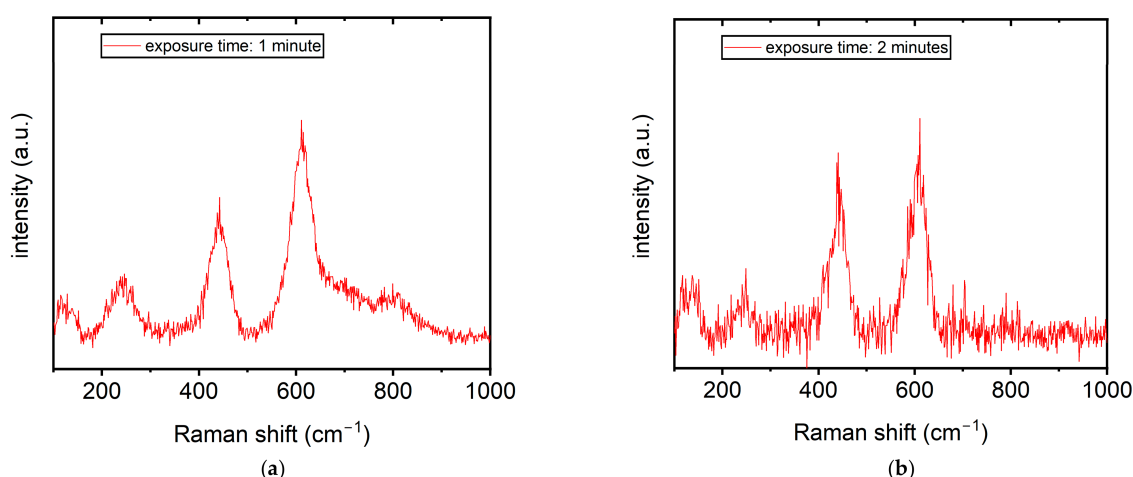


Figure 6. Representative Raman spectra collected in the middle of the cw laser-exposed area for average annealing power density of $\sim 2.5 \text{ MW/cm}^2$ for one (a) and two (b) minutes, respectively. The laser beam was focused on the surface through a $100\times$ (NA 0.85) objective lens. The acquisition time was set to 10 s. The increase in annealing time at $\sim 2.5 \text{ MW/cm}^2$ leads to the suppression of the mode at $\sim 800 \text{ cm}^{-1}$ (assigned to hydrocarbons/C–C skeletal/conformational modes).

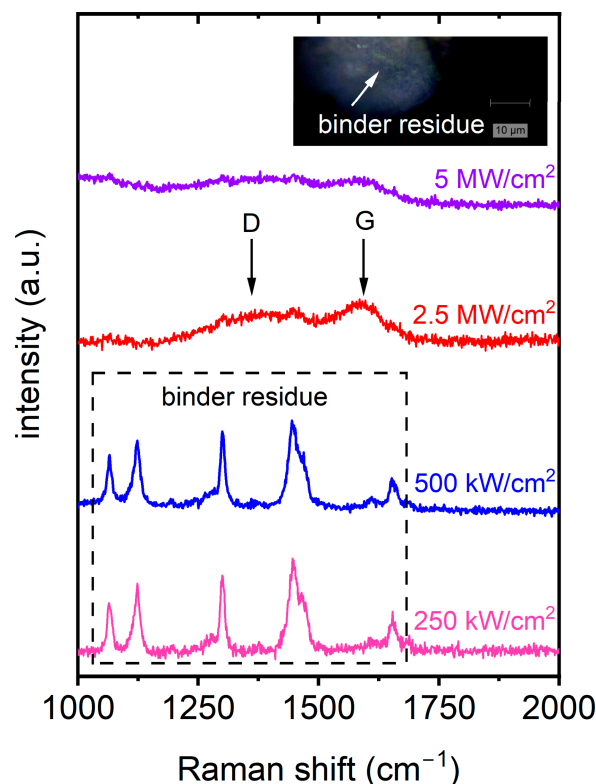


Figure 7. Representative Raman spectra were collected in the “binder-residue” region with an exposure time of one minute and average optical power densities ranging from $\sim 250 \text{ kW/cm}^2$ to $\sim 5 \text{ MW/cm}^2$. The laser beam was focused on the surface through a $100\times$ (NA 0.85) objective lens. The acquisition time was set to 10 s. The characteristic fingerprints related to the mixture of binder-related educts and decomposition products disappear after local laser annealing at $\sim 2.5 \text{ MW/cm}^2$ and above, and the characteristic D and G modes related to defective carbon evolve.

Finally, we display the results of areas that appear metallic but additionally exhibit a wavy, deformed surface, as shown in the optical micrographs presented in Figure 8 and the inset in Figure 9. The investigated target area is surrounded by wavy, deformed regions. Unlike the metallic/clean area shown in Figure 1a (before laser exposure), a metallic region was identified that did not exhibit any Raman modes within the measured range before or after laser exposure in the non-laser-annealed regions. It should be noted that this region with a metallic character and lacking the aforementioned Raman modes was chosen carefully for comparison purposes. After applying the local laser annealing procedure at an average optical power density of $\sim 5 \text{ MW/cm}^2$ for one and two minutes, a black region (black spot) becomes visible, which is then found to be Raman active. Representative Raman spectra collected before and after cw laser exposure, in the middle of the ‘black’ region (corresponding to Figure 8), are presented in Figure 9. The recorded measurement before laser annealing exhibits no visible Raman modes (black trace in Figure 9), whereas the Raman measurements after annealing reveal Raman modes related to residual organic binder system products. The broad Raman mode at $\sim 800 \text{ cm}^{-1}$ (assigned to C–C skeletal/conformational modes) that evolved after a one-minute exposure is nearly suppressed after two minutes of total laser exposure. This is clearly evident from Figure 9. The simple explanation for this effect is the thermal, laser-initiated migration of binder residue products from the deeper regions of the investigated specimens. This results in the appearance of the hydrocarbon signal in the initially pure metallic regions after laser annealing. Repeating micro-Raman measurements reproducibly confirm the presence of a broad, characteristic Raman mode at $\sim 800 \text{ cm}^{-1}$ (assigned to C–C skeletal/conformational modes) in the mea-

sured Raman spectra, which evolves after laser exposure of 5 MW/cm^2 for one minute. Further investigations and physical–chemical modeling studies are required, which will be the focus of our future work. These studies will examine the mechanisms behind the results observed in experiments. This is important for understanding how residual binder system compounds are transported from deeper layers to the surface during laser exposure. Nevertheless, the presented results provide indirect evidence of the presence of binder residues beneath the targeted region. The effect confirms that increasing the laser exposure time is the effective driving mechanism behind structural and compositional changes, analogously to what is already presented in Figure 6. Additionally, characteristic Raman modes at $\sim 155 \text{ cm}^{-1}$, $\sim 440 \text{ cm}^{-1}$ and $\sim 605 \text{ cm}^{-1}$ associated with TiC also occurred, as can be seen in Figure 9. Therefore, we can conclude that residual binder-related educts and their decomposition reaction products occurred during local “post-annealing” (initiated by laser exposure) of the investigated material.

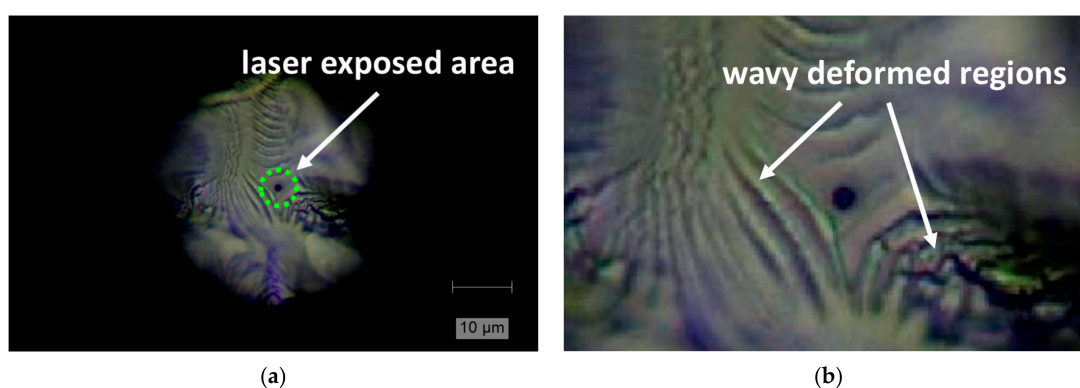


Figure 8. (a) Optical micrograph of the Ti-6Al-4V material after the laser micro-annealing procedure was performed at a single position at $\sim 5 \text{ MW/cm}^2$ for one minute. (b) A detailed view of the laser-exposed spot in the target area, surrounded by wavy deformed regions.

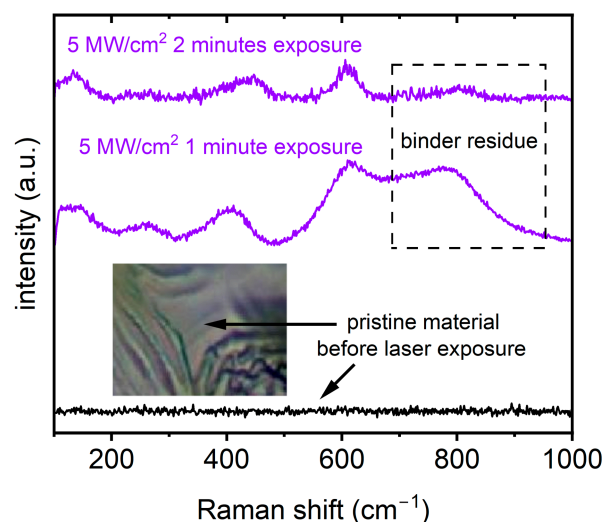


Figure 9. Representative Raman spectra were collected before and after cw laser exposure at an average optical power density of $\sim 5 \text{ MW/cm}^2$ for one and two minutes, respectively, in the middle of the ‘black’ region (see Figure 8). The laser beam was focused on the surface through a $100\times$ (NA 0.85) objective lens. The acquisition time was set to 10 s. The broad Raman mode at $\sim 800 \text{ cm}^{-1}$ (assigned to C–C skeletal/conformational modes) evolved after a one-minute exposure time and originated from binder residues in the deeper region below the central region of the pristine material. This Raman mode was nearly suppressed after two minutes of total laser exposure. The inset displays a micrograph of the pristine area.

Micro-Raman mapping intensity measurements were also carried out on the targeted Ti-6Al-4V region/on the single exposed black region, i.e., after the local laser micro-annealing procedure for one minute at an average optical power density of $\sim 5 \text{ MW}/\text{cm}^2$ (see Figure 8). The respective images of the selected Raman modes are presented in Figure 10. The highest Raman intensity was observed in the middle of the thermally transformed region for the following Raman modes: 155 cm^{-1} and 440 cm^{-1} (assigned to TiC), as well as at 800 cm^{-1} (corresponding to C–C skeletal/conformational modes). As Figure 10 shows, these results confirm the local nature of thermally laser-induced changes in all three cases. This is manifested by an abrupt decrease in intensity (micro-Raman mapping intensity images, see Figure 10) in the lateral distribution on the laser-exposed area. This observation is fully consistent with our previous studies of the structural transformation and degradation effects induced by pulsed (femtosecond) and cw laser exposure in Bi_2Se_3 nanolayers [47].

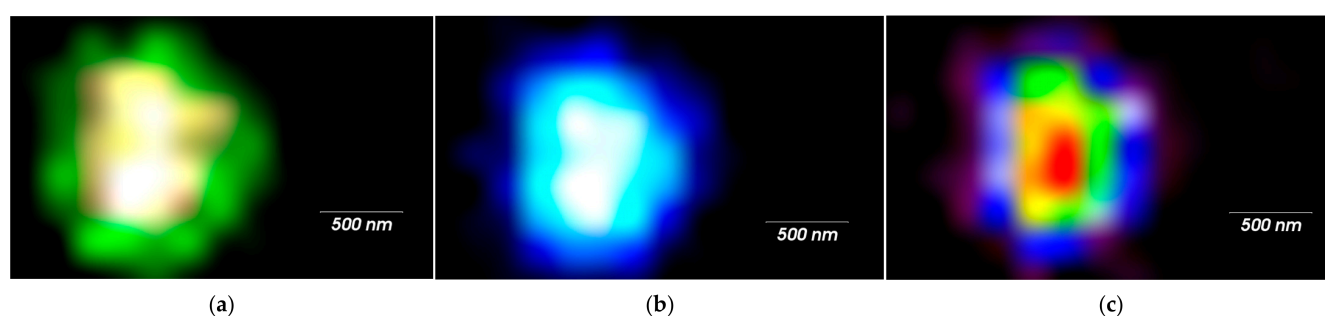


Figure 10. Micro-Raman mapping measurements were performed (from 100 cm^{-1} to 2000 cm^{-1}) on a single exposed spot where the laser-micro-annealing procedure was applied to a Ti-6Al-4V region with fully metallic character, i.e., no Raman modes were visible before exposure. Micro-Raman intensity mapping images are displayed (three characteristic peaks) as follows: (a) 155 cm^{-1} and (b) 440 cm^{-1} assigned to TiC and (c) 800 cm^{-1} assigned to C–C skeletal/conformational modes. The laser beam was focused on the surface through a $100\times$ (NA 0.85) objective lens. The average optical power density was $\sim 0.05 \text{ kW}/\text{cm}^2$. The acquisition time was set to 10 s. The mapping step size was 200 nm. The total acquisition time (measurement duration) was $\sim 7 \text{ h}$. The intensities are color-coded from the middle position (maximum) to the rim position (minimum) as follows: (a) white to yellow to green, (b) white to turquoise to blue, and (c) red to green/yellow to blue/violet. Black in all three Raman mode images means zero intensity. The localized intensities (color-coded), for all three cases, in the target region, surrounded by a black area, confirm that laser micro annealing under high $\sim 5 \text{ MW}/\text{cm}^2$ average laser power intensity for one minute (exposure time) can initialize the appearance of Raman modes related to the above-mentioned compounds stemming from the depth of the material.

4. Conclusions

In this study, the influence of laser-micro-annealing procedures performed within the power density range from approximately $0.05 \text{ kW}/\text{cm}^2$ to $5 \text{ MW}/\text{cm}^2$ on additively manufactured Ti-6Al-4V (via metal fused filament fabrication (MF³) technology) was investigated using micro-Raman spectroscopy. Generally, the specimens contain residues of the organic-based binder educts. We observed that the morphology of the specimens is non-uniform. We identified several different morphological areas which corresponded to specific spectra. These areas were studied before and after laser micro-annealing. Each area behaved uniquely, disclosing the participation of different chemical educts and the formation of different by-products in the specimen's reaction pathways during laser annealing. For metallic regions characterized initially by a weak hydrocarbon signature, the hydrocarbon signature disappears and TiC forms instead. In regions with binder residues, characterized by characteristic fingerprints related to binder-related educts and their decomposition

reaction products, the fingerprints disappear, and modes for defective carbon evolve, and a carbonization process sets in. In pure metallic regions characterized morphologically by flat areas surrounded by wavy deformed regions and by a lack of Raman modes, the annealing procedure leads to the appearance of the hydrocarbon-related mode, which disappears upon further annealing. The hydrocarbon compound most likely stems from deeper regions in the specimen. Applying laser power densities above 2.5 MW/cm^2 for up to two minutes results in the complete suppression of Raman modes related to hydrocarbons. Furthermore, exposure to average laser power densities in the range between $\sim 500 \text{ kW/cm}^2$ and $\sim 2.5 \text{ MW/cm}^2$ initiates “carbonization” processes in regions predominantly built from residual organic binder-related educts and their decomposition reaction products.

In summary, this brief study indicates that precise local heat control is essential for producing materials with consistent impurity content at the microscale. Future investigations will explore the correlation between laser-micro-annealing, microscale impurities, and mechanical properties. It cannot be excluded that an optimized laser-micro-annealing procedure could lead to favorable mechanical properties. The obtained knowledge will be important for the lifetime and reliability of future, sophisticated, micrometer-sized tools fabricated using metal fused filament fabrication (MF³) technology. The results presented here are a prerequisite, a first building block, towards developing large-array, multi-injector technology. This would enable sophisticated tools to be designed and fabricated using MF³ technology, for example, biocompatible implants with locally tuned mechanical properties as required.

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Abbreviations

The following abbreviations are used in this manuscript:

MF ³	metal fused filament fabrication
PVB	poly(vinyl butyral)
PEG	polyethylene glycol
ATBC	acetyltributyl citrate

References

1. Xu, Y.; Lu, Y.; Sundberg, K.L.; Liang, J.; Sisson, R.D. Effect of Annealing Treatments on the Microstructure, Mechanical Properties and Corrosion Behavior of Direct Metal Laser Sintered Ti-6Al-4V. *J. Mater. Eng. Perform.* **2017**, *26*, 2572–2582. [[CrossRef](#)]
2. Deng, Q.; Wu, Y.; Zhu, W.; Chen, K.; Liu, D.; Peng, L.; Ding, W. Effect of Heat Treatment on Microstructure Evolution and Mechanical Properties of Selective Laser Melted Mg-11Gd-2Zn-0.4Zr Alloy. *Mater. Sci. Eng. A* **2022**, *829*, 142139. [[CrossRef](#)]

3. Jaber, H.; Kónya, J.; Kulcsár, K.; Kovács, T. Effects of Annealing and Solution Treatments on the Microstructure and Mechanical Properties of Ti6Al4V Manufactured by Selective Laser Melting. *Materials* **2022**, *15*, 1978. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Wang, D.; Wang, H.; Chen, X.; Liu, Y.; Lu, D.; Liu, X.; Han, C. Densification, Tailored Microstructure, and Mechanical Properties of Selective Laser Melted Ti–6Al–4V Alloy via Annealing Heat Treatment. *Micromachines* **2022**, *13*, 331. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Luo, Y.; Wang, M.; Zhu, J.; Tu, J.; Jiao, S. Microstructure and Corrosion Resistance of Ti6Al4V Manufactured by Laser Powder Bed Fusion. *Metals* **2023**, *13*, 496. [\[CrossRef\]](#)
6. Rietema, C.J.; Roehling, J.D.; Smith, W.L.; Bertsch, K.M. Microstructural Control of Additively Manufactured Ti6Al4V via In-Situ Large-Area Laser Annealing. *Scr. Mater.* **2024**, *239*, 115823. [\[CrossRef\]](#)
7. Usha Rani, S.; Sadhasivam, M.; Kesavan, D.; Pradeep, K.G.; Kamaraj, M. A Multi-Scale Microscopic Study of Phase Transformations and Concomitant α/β Interface Evolution in Additively Manufactured Ti-6Al-4V Alloy. *Mater. Sci. Eng. A* **2024**, *900*, 146400. [\[CrossRef\]](#)
8. Wang, M.; Yan, H.; Lu, Q.; Zhang, P.; Liu, K. Selective Laser Melted Ti-6Al-4V Alloy after Post-Heat Treatments: Microstructure, Mechanical Properties and Fatigue Behavior. *J. Mater. Eng. Perform.* **2025**, *34*, 5381–5393. [\[CrossRef\]](#)
9. Li, C.; Tao, Y.; Zhang, Y.Z.; Wu, Z.; Zhang, S.Y.; Zhang, P.; Chen, W. Effect of Annealing Treatment on Microstructure and Properties of Low-Cost Selective Laser Melting HDH Ti6Al4V. *J. Mater. Sci.* **2025**, *60*, 13011–13028. [\[CrossRef\]](#)
10. Dash, S.S.; Liu, Z.; Lang, L.; Lyu, T.; Chen, D.; Zou, Y. Laser-Based Direct Energy Deposition of Compositionally Graded Titanium Alloys: Microstructural Evolution, Hardness, and Tensile Properties. *J. Alloys Compd.* **2025**, *1020*, 179335. [\[CrossRef\]](#)
11. Tan, J.; Peng, H.; Yuan, J.; Wang, W.; Wang, B. Mechanical Properties and Microstructure of a Ti-6Al-4V Alloy via Asynchronous Laser Welding. *Mater. Lett.* **2026**, *420*, 141172. [\[CrossRef\]](#)
12. Cao, S.; Zou, Y.; Lim, C.V.S.; Wu, X. Review of Laser Powder Bed Fusion (LPBF) Fabricated Ti-6Al-4V: Process, Post-Process Treatment, Microstructure, and Property. *Light Adv. Manuf.* **2021**, *2*, 1. [\[CrossRef\]](#)
13. Zhang, C.; Zou, D.; Mazur, M.; Mo, J.P.T.; Li, G.; Ding, S. The State of the Art in Machining Additively Manufactured Titanium Alloy Ti-6Al-4V. *Materials* **2023**, *16*, 2583. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Deng, H.; Liu, W.; Zhou, L.; Cao, S.; Chen, L. *Post-Process Treatments for Additive Manufactured Titanium Alloys*; IntechOpen: London, UK, 2024. [\[CrossRef\]](#)
15. Ye, Y.; Zhang, Y.; Wang, K.; Gao, L.; Huang, T.; Wang, J.; Yang, H.; Ye, C.; Ding, H. Post-Processing of Additively Manufactured Ti64 Alloy Using Electropulsing-Assisted Ultrasonic Nanocrystal Surface Modification. *Mater. Charact.* **2025**, *228*, 115413. [\[CrossRef\]](#)
16. Puspashree, A.; Sahoo, A.K.; Panda, A.; Kumar, R. Fabrication, Characterization, and Post-Processing Machinability Aspects of Additively Manufactured Titanium Alloys: A Review of Industrial Challenges and Cleaner Strategies. *Proc. Inst. Mech. Eng. Part E J. Process Mech. Eng.* **2026**. [\[CrossRef\]](#)
17. Tebianian, M.; Hosseini, S.R.E.; Mohammadi, S.A.M.; Farbakhti, M.; Sadeghi, B.M.; Jafari, N.S.R.; Yuan-ming, H.; Li, R. Mechanical Properties of Titanium Alloys Produced by Additive Manufacturing: A Review. *Met. Mater. Int.* **2026**, *32*, 1778–1808. [\[CrossRef\]](#)
18. Uriondo, A.; Esperon-Miguez, M.; Perinpanayagam, S. The Present and Future of Additive Manufacturing in the Aerospace Sector: A Review of Important Aspects. *Proc. Inst. Mech. Eng. G J. Aerosp. Eng.* **2015**, *229*, 2132–2147. [\[CrossRef\]](#)
19. Dejene, N.D.; Lemu, H.G. Current Status and Challenges of Powder Bed Fusion-Based Metal Additive Manufacturing: Literature Review. *Metals* **2023**, *13*, 424. [\[CrossRef\]](#)
20. Papynov, E.K.; Shichalin, O.O.; Belov, A.A.; Buravlev, I.Y.; Mayorov, V.Y.; Fedorets, A.N.; Buravleva, A.A.; Lembikov, A.O.; Gritsuk, D.V.; Kapustina, O.V.; et al. CaSiO₃-HAp Metal-Reinforced Biocomposite Ceramics for Bone Tissue Engineering. *J. Funct. Biomater.* **2023**, *14*, 259. [\[CrossRef\]](#) [\[PubMed\]](#)
21. Jacob, J.; Pejak Simunec, D.; Kandjani, A.E.Z.; Trinci, A.; Sola, A. A Review of Fused Filament Fabrication of Metal Parts (Metal FFF): Current Developments and Future Challenges. *Technologies* **2024**, *12*, 267. [\[CrossRef\]](#)
22. Young, R.T.; White, C.W.; Clark, G.J.; Narayan, J.; Christie, W.H.; Murakami, M.; King, P.W.; Kramer, S.D. Laser Annealing of Boron-implanted Silicon. *Appl. Phys. Lett.* **1978**, *32*, 139–141. [\[CrossRef\]](#)
23. Celler, G.K.; Poate, J.M.; Kimerling, L.C. Spatially Controlled Crystal Regrowth of Ion-implanted Silicon by Laser Irradiation. *Appl. Phys. Lett.* **1978**, *32*, 464–466. [\[CrossRef\]](#)
24. Baeri, P.; Campisano, S.U.; Foti, G.; Rimini, E. A Melting Model for Pulsing-laser Annealing of Implanted Semiconductors. *J. Appl. Phys.* **1979**, *50*, 788–797. [\[CrossRef\]](#)
25. Mikulics, M.; Kordoš, P.; Gregušová, D.; Sofer, Z.; Winden, A.; Trellenkamp, S.t.; Moers, J.; Mayer, J.; Hardtdegen, H. Conditioning Nano-LEDs in Arrays by Laser-Micro-Annealing: The Key to Their Performance Improvement. *Appl. Phys. Lett.* **2021**, *118*, 043101. [\[CrossRef\]](#)
26. Lee, C.; Srisungsitthisunti, P.; Park, S.; Kim, S.; Xu, X.; Roy, K.; Janes, D.B.; Zhou, C.; Ju, S.; Qi, M. Control of Current Saturation and Threshold Voltage Shift in Indium Oxide Nanowire Transistors with Femtosecond Laser Annealing. *ACS Nano* **2011**, *5*, 1095–1101. [\[CrossRef\]](#) [\[PubMed\]](#)

27. Kim, S.; Kim, S.; Srisungsitthisunti, P.; Lee, C.; Xu, M.; Ye, P.D.; Qi, M.; Xu, X.; Zhou, C.; Ju, S.; et al. Selective Contact Anneal Effects on Indium Oxide Nanowire Transistors Using Femtosecond Laser. *J. Phys. Chem. C* **2011**, *115*, 17147–17153. [CrossRef]
28. Kwon, H.; Choi, W.; Lee, D.; Lee, Y.; Kwon, J.; Yoo, B.; Grigoropoulos, C.P.; Kim, S. Selective and Localized Laser Annealing Effect for High-Performance Flexible Multilayer MoS₂ Thin-Film Transistors. *Nano Res.* **2014**, *7*, 1137–1145. [CrossRef]
29. Ha, J.; Lee, B.J.; Hwang, D.J.; Kim, D. Femtosecond Laser Nanowelding of Silver Nanowires for Transparent Conductive Electrodes. *RSC Adv.* **2016**, *6*, 86232–86239. [CrossRef]
30. Mikulics, M.; Lu, J.G.; Huang, L.; Tse, P.L.; Zhang, J.Z.; Mayer, J.; Hardtdegen, H. Laser Micro Annealing Conditioning for the Suppression of Statistical Scatter in Freestanding Sb₂Te₃ Nanowire Resistance. *FlatChem* **2020**, *21*, 100164. [CrossRef]
31. Edwards, H.G.M. *Handbook of Vibrational Spectroscopy—Spectra–Structure Correlations in Raman Spectroscopy*; Chalmers, J.M., Griffiths, P.R., Eds.; John Wiley & Sons Ltd.: Hoboken, NJ, USA, 2001. [CrossRef]
32. Hiejima, Y.; Kida, T.; Takeda, K.; Igarashi, T.; Nitta, K. Microscopic Structural Changes during Photodegradation of Low-Density Polyethylene Detected by Raman Spectroscopy. *Polym. Degrad. Stab.* **2018**, *150*, 67–72. [CrossRef]
33. Andrikopoulos, K.S.; Yannopoulos, S.N.; Kolobov, A.V.; Fons, P.; Tominaga, J. Raman Scattering Study of GeTe and Ge₂Sb₂Te₅ Phase-Change Materials. *J. Phys. Chem. Solids* **2007**, *68*, 1074–1078. [CrossRef]
34. Němec, P.; Nazabal, V.; Moreac, A.; Gutwirth, J.; Beneš, L.; Frumar, M. Amorphous and Crystallized Ge–Sb–Te Thin Films Deposited by Pulsed Laser: Local Structure Using Raman Scattering Spectroscopy. *Mater. Chem. Phys.* **2012**, *136*, 935–941. [CrossRef]
35. Bragaglia, V.; Holldack, K.; Boschker, J.E.; Arciprete, F.; Zallo, E.; Flissikowski, T.; Calarco, R. Far-Infrared and Raman Spectroscopy Investigation of Phonon Modes in Amorphous and Crystalline Epitaxial GeTe-Sb₂Te₃ Alloys. *Sci. Rep.* **2016**, *6*, 28560. [CrossRef] [PubMed]
36. Ogura, A.; Yamasaki, K.; Kosemura, D.; Tanaka, S.; Chiba, I.; Shimidzu, R. UV-Raman Spectroscopy System for Local and Global Strain Measurements in Si. *Jpn. J. Appl. Phys.* **2006**, *45*, 3007. [CrossRef]
37. Mikulics, M.; Sofer, Z.; Winden, A.; Trellenkamp, S.; Förster, B.; Mayer, J.; Hardtdegen, H.H. Nano-LED Induced Chemical Reactions for Structuring Processes. *Nanoscale Adv.* **2020**, *2*, 5421–5427. [CrossRef] [PubMed]
38. Mikulics, M.; Hardtdegen, H.; Mayer, J. Device for Photon-Induced Processes and/or Modifications of Materials. European Patent Application EP4137229A1, 15 June 2022.
39. Ahmad, M.A.; Jabir, M.; Johari, N.; Ibrahim, R.; Hamidi, N. The Effect of Impurities Elements on Titanium Alloy (Ti-6Al-4V) MIM Sintered Part Properties. *AIP Conf. Proc.* **2017**, *1901*, 040007. [CrossRef]
40. Winkler, K.; Seidel, P.; Danzig, A.; Kroll, L.; Undisz, A. Influence of Carbon on Additively Manufactured Ti-6Al-4V. *J. Manuf. Mater. Process.* **2023**, *7*, 134. [CrossRef]
41. Winkler, K.; Ahmad, H.; Danzig, A.; Gloetter, P.; Schubert, F.; Wagner, G.; Kroll, L. Effect of Organic Impurity in Additive Manufactured Ti-6Al-4V. *Addit. Manuf. Lett.* **2023**, *5*, 100116. [CrossRef]
42. Eickhoff, R.; Antusch, S.; Nötzel, D.; Hanemann, T. Metal Fused Filament Fabrication (MF3) of Ti-6Al-4 V Implants by Using Flexible, Partially Water-Soluble Binder Systems. *Mater. Des.* **2025**, *254*, 114088. [CrossRef]
43. Eickhoff, R.; Antusch, S.; Tesari, I.; Mikulics, M.; Hardtdegen, H.H.; Nötzel, D.; Kutlu, A.; Hanemann, T. Influence of the Layer Orientation and the Binder System on the Mechanical Behavior of Titanium Components Manufactured by Metal Fused Filament Fabrication (MF3). *Mater. Sci. Eng. A* **2026**, *975*, 150905. [CrossRef]
44. Mikulics, M.; Adam, R.; Chen, G.; Chakraborty, D.; Cheng, J.; Pericolo, A.; Komissarov, I.; Bürgler, D.E.; Heidtfeld, S.F.; Serafini, J.; et al. Determination of Thermal Damage Threshold in THz Photomixers Using Raman Spectroscopy. *Crystals* **2023**, *13*, 1267. [CrossRef]
45. Ahrens, L.; Mikulics, M.; Schröder, S.; Mayer, J.; Hardtdegen, H.H. Laser-Micro-Annealing of Microcrystalline Ni-Rich NCM Oxide: Towards Micro-Cathodes Integrated on Polyethylene Terephthalate Flexible Substrates. *Materials* **2025**, *18*, 680. [CrossRef] [PubMed]
46. Reimers, J.; Mikulics, M.; Lipinska-Chwalek, M.; Zeller-Plumhoff, B.; Kibkalo, L.; Kruth, M.; Willumeit-Römer, R.; Mayer, J.; Hardtdegen, H.H. Towards Correlative Raman Spectroscopy–STEM Investigations Performed on a Magnesium–Silver Alloy FIB Lamella. *Nanomaterials* **2025**, *15*, 430. [CrossRef] [PubMed]
47. Adam, R.; Mikulics, M.; Bürgler, D.E.; Niherysh, K.A.; Kalaboukhov, A.; Heidtfeld, S.F.; Komissarov, I.; Sobolewski, R.; Schneider, C.M.; Mayer, J.; et al. Laser-Induced Degradation of Bi₂Se₃ THz Emitters Revealed by Raman Spectroscopy. *Photonics* **2026**, *13*, 278. [CrossRef]
48. Steigerwal, W. Key Building Block for Organic Molecules Discovered in Meteorites. Available online: <https://www.nasa.gov/solar-system/key-building-block-for-organic-molecules-discovered-in-meteorites/> (accessed on 18 December 2020).
49. Kaiser, K.; Schulz, F.; Maillard, J.F.; Hermann, F.; Pozo, I.; Peña, D.; Cleaves, H.J.; Burton, A.S.; Danger, G.; Afonso, C.; et al. Visualization and Identification of Single Meteoritic Organic Molecules by Atomic Force Microscopy. *Meteorit. Planet. Sci.* **2022**, *57*, 644–656. [CrossRef] [PubMed]

50. Johnston, C.O.; Stern, E.C.; Wheeler, L.F. Radiative Heating of Large Meteoroids during Atmospheric Entry. *Icarus* **2018**, *309*, 25–44. [[CrossRef](#)]
51. Leiser, D.; Dürnhöfer, C.; Poloni, E.; Löhle, S.; Matlovič, P.; Tóth, J.; Vaubaillon, J. Meteorite Temperature Measurements during Ground Testing. *Icarus* **2024**, *408*, 115867. [[CrossRef](#)]
52. Strobl, G.R.; Hagedorn, W. Raman Spectroscopic Method for Determining the Crystallinity of Polyethylene. *J. Polym. Sci. Polym. Phys. Ed.* **1978**, *16*, 1181–1193. [[CrossRef](#)]
53. Lagaron, J.M. On the Use of a Raman Spectroscopy Band to Assess the Crystalline Lateral Packing in Polyethylene. *J. Mater. Sci.* **2002**, *37*, 4101–4107. [[CrossRef](#)]
54. Lohse, B.H.; Calka, A.; Wexler, D. Raman Spectroscopy as a Tool to Study TiC Formation during Controlled Ball Milling. *J. Appl. Phys.* **2005**, *97*, 114912. [[CrossRef](#)]
55. Kaipoldayev, O.; Mukhametkarimov, Y.; Nemkaeva, R.; Baigarinova, G.; Aitzhanov, M.; Muradov, A.; Guseinov, N. Studying of 2D Titanium Carbide Structure by Raman Spectroscopy after Heat Treatment in Argon and Hydrogen Atmospheres. *Eurasian Chem.-Technol. J.* **2017**, *19*, 181. [[CrossRef](#)]
56. Klein, M.V.; Holy, J.A.; Williams, W.S. Raman Scattering Induced by Carbon Vacancies in TiC_x. *Phys. Rev. B* **1978**, *17*, 1546–1556. [[CrossRef](#)]
57. Ait Djafer, A.Z.; Saoula, N.; Madaoui, N.; Zerizer, A. Deposition and Characterization of Titanium Carbide Thin Films by Magnetron Sputtering Using Ti and TiC Targets. *Appl. Surf. Sci.* **2014**, *312*, 57–62. [[CrossRef](#)]
58. De Bonis, A.; Santagata, A.; Galasso, A.; Laurita, A.; Teghil, R. Formation of Titanium Carbide (TiC) and TiC@C Core-Shell Nanostructures by Ultra-Short Laser Ablation of Titanium Carbide and Metallic Titanium in Liquid. *J. Colloid Interface Sci.* **2017**, *489*, 76–84. [[CrossRef](#)] [[PubMed](#)]
59. Vasanthakumar, K.; Bakshi, S.R. Effect of C/Ti Ratio on Densification, Microstructure and Mechanical Properties of TiC_x Prepared by Reactive Spark Plasma Sintering. *Ceram. Int.* **2018**, *44*, 484–494. [[CrossRef](#)]
60. Urbonaite, S.; Hålldahl, L.; Svensson, G. Raman Spectroscopy Studies of Carbide Derived Carbons. *Carbon N. Y.* **2008**, *46*, 1942–1947. [[CrossRef](#)]
61. Fan, Q.; Wang, H.; Song, Y.; Zhang, W.; Yun, S. Five Carbon Allotropes from Squaroglitter Structures. *Comput. Mater. Sci.* **2020**, *178*, 109634. [[CrossRef](#)]
62. Schuepfer, D.B.; Badaczewski, F.; Guerra-Castro, J.M.; Hofmann, D.M.; Heiliger, C.; Smarsly, B.; Klar, P.J. Assessing the Structural Properties of Graphitic and Non-Graphitic Carbons by Raman Spectroscopy. *Carbon N. Y.* **2020**, *161*, 359–372. [[CrossRef](#)]

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