

## Laser-Thermochemical Induced Micro-Structures on Titanium

## Sandro Eckert<sup>1</sup> . Hamza Messaoudi<sup>1</sup> . Salar Mehrafsun<sup>1</sup> . Frank Vollertsen<sup>1,2</sup>

<sup>1</sup>BIAS - Bremer Institut für angewandte Strahltechnik, Klagenfurter Str. 5, 28359 Bremen, Germany. <sup>2</sup>University of Bremen, Faculty of Production Engineering - Mechanical Engineering & Process Engineering, Badgasteiner Strasse 1, 28359 Bremen, Germany.

#### ABSTRACT

Laser thermochemical machining is a non-conventional processing method that unifies the advantages of laser machining with its precise and localized energy deposition and electrochemical machining with its gentle removal quality without significant thermal impacts. In this work, titanium samples are processed by a cw-laser irradiation in a closed chamber flowed through phosphoric acid with the aim to study the influence on the chemical composition in the machined zone. To identify the upper thermochemical process limit comparative investigations are performed in deionized water and argon environments. Therefore, the resulting structure sizes and shapes are characterized in dependence of laser power and focus diameter using laser and electron scanning microscopy. With a focal spot of  $30 \ \mu m$  and an irradiation time of  $1 \ s$  it is shown that a disturbance-free surface modification without affecting the chemical composition is observed for laser powers between 0.7 W and 1.3 W. A further increase of laser power results in the occurrence of removal disturbances. From prepared cross-sections and EDX-measurements it is shown that, these disturbances consist of low soluble titanium-phosphate and titanium-oxide compounds. The detected titanium-phosphate is a result of the deposition of phosphate during the chemical reaction. Its formation and growth to upstanding micro-structures is discussed in terms of the temperature induced reaction dynamics. Furthermore, it is shown that these structures can be tuned in size by the focal beam diameter as well as reproduced over a macroscopic large area by selective scanning for surfaces structuring. © 2017 IMSSE and Science IN. All rights reserved

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## Introduction

Titanium and titanium-based shaped memory alloys such as Nitinol are increasingly used in chemical and medical applications. This is due to their high corrosion resistance and biocompatibility [1], which is based on the titaniumdioxide layer that covers the titanium as soon as it gets in contact with oxygen. For biomedical devices a gentle and selective micro material processing [2] with smooth surface properties and especially for shaped memory alloys low thermal impact is required [3]. Often used short-pulsed laser processes produce a significant material heating, solidified ablation debris and recast layer during the machining [4]. Consequently, not only the component functionality can be reduced because of the affected material properties but also the application of additional manufacturing steps such as electro polishing or heat treatment procedures are often necessary.

In contrast, the laser induced thermochemical machining avoids these negative effects by combining the selective laser processing with a chemical material removal [5]. Thereby, the chemical material removal is based on an etching process, which ensures a high surface quality down to a roughness below 0.1  $\mu$ m [6]. Due to its natural oxygen layer, titanium is passivated in an acid electrolyte ambient and shows no material corrosion. This changes drastically while the laser radiation locally heats up the surface. On the one hand, the Flade potential is shifted with increasing temperature and there by the chemical etching reaction, described in Eq. 1, can be initiated. On the other hand, the chemical reaction is enhanced by orders of magnitude due to the changed Nernst potential [7]. Thus, the titanium loses its natural passivation property [8] and a local

material dissolution takes place following the chemical reaction:

$$2 H_2 PO_4^- + Ti \to 2 HPO_4^{2^-} + Ti^{2^+} + H_2$$
(1)

This allows a precise and selective micro machining of the workpiece. At least the induced temperature must be high enough to shift the Flade potential to the active regime, where a material dissolution takes place. For titanium in 5 molar phosphoric acid this happens at temperatures below the boiling point. The Potential of this process for micro machining different materials [8], as well as its limits by occurring disturbances at higher laser power [9] had been shown by investigations on electrolyte-jet based setup. Typical material removal rates up to  $10 \,\mu$ m/s were reported [9].

In this work, a new laser-scanner based setup for laser chemical machining is presented following the aim to further increase the process speed and accuracy. Using this setup the material dissolution of titanium (Grade 1) in phosphoric acid is investigated within 1s-laser irradiation in dependence of laser power and spot diameter in order to identify the conditions for a stable and controllable surface modification. With increasing laser power the single spot removal is first characterized by regular Gaussian-like cavities, followed by the formation of upstanding mushroom-like structures, which changes after the upper limit for a thermochemical-driven processing into circular flat structures. Based on the induced temperature, starting material dissolution, convective electrolyte flow and boiling dynamic, a processing regime with deposition of phosphor is characterized and discussed besides a Gaussian-like material removal. Both processing regimes can be used for a precise, gentle and reproducible surface



Corresponding Author: Sandro Eckert, Tel: +49 421 218 58068 Email: Eckert@bias.de

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Figure 1: Schematic illustration of the scanner based setup for selective laser processing in wet-etching environment



Figure 2: Topographic images of the surface modification (a), (b) and their cross-section in x- and y-direction (c), (d)

modification with regard fabricate potential to functionalized surfaces.

#### Process parameter and methodology

To characterize the material removal for different laser powers P from 0.2 W up to 14 W (depending on the spot size, as summarized in Table 1) arrays of 5 x 5 single irradiation spots were structured in a phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), water (H<sub>2</sub>O) and argon (Ar) ambient. The beam diameter was varied from 30 µm to 156 µm. Thereby, the irradiation time t<sub>L</sub> was kept constant at 1 s.

**Table 1**: Overview of the varied laser process parameters

Focus diameter	Power	Intensity	
[µm]	range [W]	[kW/cm <sup>2</sup> ]	
30	0.2 - 4,0	53 - 1060	
41	0,4 - 5,0	61 - 757	
68	1,3 - 10,5	72 – 578	
109	2,5 - 11,5	54 - 246	
156	2,5 - 14,0	26 - 146	

After laser chemical machining the samples were cleaned for 5 min in an ultrasonic ethanol-bath. Afterwards the structured surface modifications were topographically characterized by using the confocal laser-scanning microscope (Keyence VK-9710) as shown in Fig. 2(a). The cavity area and depth were measured for six different irradiation spots per laser power from the LSM-images to define their errors by the standard deviation  $\pm \sigma$ . Therefore, a MATLAB script measures the horizontal and vertical cavity width in the cross-section as well as the height in the cavity center, as can be seen in Fig. 2(b-d). Furthermore, scanning electron microscopy images (Zeiss EVO MA10) were taken under a tilting angle of 65° for a detailed investigation of the shape and morphology of the

## **Experimental**

#### Experimental setup for laser chemical machining

To use the laser induced chemical material dissolution as a gentle micro machining process it is necessary to ensure a controllable and disturbance-free laser energy deposition on the workpiece by taking into account the propagation through the liquid etchant environment. In this work the workpiece is mounted in an etching chamber, where a 5 molar (28.7 % vol.) phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) is pumped as a cross-jet through a  $(25 \times 2)$  mm<sup>2</sup> cross-section with velocity vf of 2 m/s. This allows on the one hand the use of a galvano-scanner system and on the other hand ensures a fast evacuation of emerging process gases out of the focus area, as shown in Fig. 1(a). As laser source the fibre laser JK400 is used. Its TEM<sub>00</sub> cw-laser radiation of 1080 nm is focused by a telecentric f-theta optic and guided using the scanning system Raylase Super scan III-15 to the surface. The focused laser radiation locally heats up the surface and the chemical dissolution, which shows initiates schematically Fig. 1(b). By using an inverse mounted telescope, the laser beam diameter can be reduced to one third and there by the focal spot size as well as the heated area are enlarged. As sample material rolled titanium (Grade 1) sheets of 0.8 mm thickness with a surface roughness  $S_a$  of  $(371 \pm 31)$  nm are used.

surface structures. With the installed Bruker detector, further EDX-measurements were carried out to identify the chemical compositions of the surface modifications. The element spectra were taken over 210 s on selected positions.

#### Results

# Correlation between the laser power and modification size

To use the thermochemical material dissolution in a scanner based experimental setup for large area surface structuring it is necessary to identify the process thresholds as well as to understand the influence of the process parameters on the material modifications. Therefore, in a first step the morphology, i.e. modification area A and cavity height h were investigated by laser optical microscopy.



Figure 3: Modification area over laser power for different ambient medium (red, blue, black)



**Figure 4**: Cavity depth over laser power for different ambient medium (red, blue, black) and the corresponding SEM images from Figure 5 from (1) to (6)

Figure 3 shows exemplarily the development of the modified surface area A structured in phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, red), water (H<sub>2</sub>O, blue) and argon (Ar, black) in dependence of the applied laser power using the focal spot diameter of 30 µm. In phosphoric acid a surface modification can be detected first at a laser power of 0.6 W. For  $0.6 \text{ W} > P_L > 1.3 \text{ W}$ , the modified area A increases nearly linear, while for  $P_L > 1.3$  W the modification area continues growing but with a different functional trend. In contrast to the phosphoric acid, a surface modification in deionized water is observed first at laser power of 1.2 W and its area size A remains below  $10^3 \mu m^2$  up to P<sub>L</sub> = 2.2 W. Above  $2.2\ W$  a significant and steady increase of the modification area can be observed in both ambients water and argon. The changes in the function altrend of the modification area over the laser power correlate in good agreement to appearing differences in the cavity height. Fig. 4 shows the depth of the cavity center h over the applied laser power P in the different ambient conditions. Negative values represent a material removal below the surface normal and positive values an elevated structure in the cavity center. In phosphoric acid (Fig. 4, red), no material modification is detected for a laser power below 0.6 W at an irradiation time of 1 s. However, between 0.6 W to 1.2 W the height of the etched cavities decreases linearly with the laser power down to -10  $\mu m.$  Above 1.2 W the height in the cavity center abruptly jumps back to the surface normal. Between 1.2 W and 2.2 W the cavity center elevates the surface normal with a maximum of  $+9 \,\mu\text{m}$  at 1.7 W. For a laser power higher than 2.2 W the cavity center decreases again below the surface normal. In comparison, under deionized water a slight elevation can be observed for laser powers between 1.2 W and 2.2 W, whereas no structure elevation was measured for the structuring under argon ambient. Furthermore, for P > 2.2 W, a cavity formation takes places in both media, as can be seen in Fig. 4(blue, black).

#### SEM investigation of the modification morphology

Since the laser scanning microscope images show only the surface topography from a top view, undercuts of the elevated surface structures cannot be recognized. As seen in Fig. 2(c,d), this is often indicated by an almost perpendicular drop in the topographic cross-section image. For a detailed analysis of surface elevations and cavities, the SEM-images of the different morphology regimes were performed under a tilting angle of 65°. The SEM-images in Fig. 5show the evolution of surface modifications structured in phosphoric acid with a focal diameter of 30 µm with respect to laser power. These correspond to the measurement points shown in Fig. 4. The surface modifications, except the cavity observed in Fig. 5(1) at a laser power of 0.8 W, show a material accumulation inside the cavity. At a laser power of 1.3 W (Fig. 5(2)) the observed accumulation in the cavity center shows a hemispherical shape. The recording less than 65°-angle allows showing the shape change of the formed structures into an upstanding mushroom-like one at further increased laser powers. Fig. 5(3-5) reveals that for  $1.6 \text{ W} < P_L < 2.2 \text{ W}$ these structures widen and flatten. In Fig. 5(6)at 2.8 W the surface modification appears more as a circular ditch and does not elevate the surface anymore.

By changing the focal spot diameter from  $30 \ \mu m$  to 41, 68, 109 and  $156 \ \mu m$  surface modification of similar morphology but magnified accordingly emerge. Thereby, the size of these structures increases with the focal spot diameters. Fig. 6(1-5) shows these hemispherical accumulations for different focal spot diameters at the lowest laser power, at which they were observed. With larger spot sizes, the surface modification (both, the regular cavities and the surface elevation) occurs at a higher laser power from 1.3 W up to 6.3 W. In contrast, the corresponding peak intensity I<sub>0</sub>decreases for increasing spot diameter from  $331 \ \text{kW/cm}^2$  down to  $66 \ \text{kW/cm}^2$ .

Using the scanner based setup it is possible to process larger surface areas in a reproducible and precise manner through a sequential structuring. Fig. 7(a) shows a regular surface structuring of  $30 \,\mu\text{m}$  wide cavities whereas Fig. 7(b) shows a periodic fabrication of hemispherical accumulated microstructures. Such a periodic structure arrangements change the tribological surface properties and can be used to reduce crack formation or as lubricant

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Figure 5: SEM images of the modified titanium surface for different laser power







Figure7: Surface structuring by selective scanning and reproducing the surface modification over larger areas

dent in deep drawing processes [10] as well as for flowoptimization in chemical, motor- or jet-engine applications.

#### EDX analysis of the surface elevations

Figure 8 shows EDX-measurements of the chemical composition of the different surface modifications. Within the disturbance-free cavities, whose EDX-spectrum is colored black, only the typical titanium peaks  $K_{\alpha}$  and  $K_{\beta}$  could be identified (Fig. 8, black). In contrast, the spectrum of the hemispherical accumulated microstructures shows for a laser power of 1.3 W significant phosphor and oxygen peaks besides the titanium (Fig. 8, red). The further elevated microstructures at a laser power of 1.5 W shows on the one hand at the red marked position the same material composition as before and on the other hand on its top at the blue marked position a different material composition. The blue spectrum shows mainly titanium and oxygen components while the red spectrum contains a significant proportion of phosphor.

In addition, the chemical composition of the accumulated surface modifications and the different phases of these structures were investigated in the cross-section shown in



Figure 8: EDX-spectrum of different surface structures

Fig. 9. For reason of better sample preparation the surface modification structured at 4.5 W with the 109  $\mu m$  focal diameter was selected. As can be seen in Fig. 9, the base-material titanium can be clearly distinguished from the

titanium-phosphorus-oxygen phase marked in red and titanium-oxygen phase marked in blue in accordance to the red and blue spectrum in Fig. 8. The etched cavity is confined by a phase boundary to the titanium-phosphorusoxygen phase. The mushroom-like piled up surface modification consists mainly of the titanium-phosphorusoxygen composite. Further, a thin titanium-oxide layer seems to cover the whole surface with a thick accumulation on the top of this surface modification.



Figure 9: Cross-section of a surface structure with its different phases

#### **Discussion**

Based on the investigation of the modification area A (Fig. 3) and the center removal depth h (Fig. 4) the following different processing regimes were classified for a focal spot diameter of  $30 \ \mu m$  in phosphoric acid:

- Regular cavities with linear decreasing height: 0.6 W < P  $\leq$  1.2 W
- Elevating material accumulation inside the cavities: 1.3 W  $\leq$  P  $\leq$  2.2 W
- $\bullet$  Flat circular ditches below the surface normal: P > 2.2 W

The formation of the regular cavities is the result of the laser thermal-induced electrochemical etching process described by the chemical reaction according to Eq. 1. This process is initiated by the temperature gradient between the laser beam center and its periphery, which creates an electrochemical potential difference and leads to a local material etching [12]. This is characterized by an extremely enhanced chemical dissolution reaction that speeds up to  $10^3$  magnitudes with increasing temperatures [7]. Depending on the applied laser energy, the removal rates can rise up to  $10 \,\mu$ m/s, which was reported by Nowak et al. [9] as the upper limit of the etching process. Similar maximum etching rates were obtained in this work, as can be seen from Fig. 4. This limitation can be explained by emerging process gases and boiling effects [11] since the surface temperature can quickly exceed the boiling temperature of the electrolyte [13]. The reaction at the acid-metal-interface generates hydrogen gas as tiny bubbles that can adhere to the surface and slow down the reaction by preventing an acid/metal contact. As a consequence of this shielding removal disturbances can occur and result in the formation of irregular structures similar to the here reported ones.

As the observed surface modification can exceed the surface normal, as shown in Fig. 4, gas bubble shielding could not be the only explanation of this observation. The EDX-Analysis in Fig. 8 and Fig. 9 reveals that the observed surface elevations (Fig. 5) are also related to additional laser thermo-chemical and fluid dynamic processes. The presented results can be explained by the laser-enhanced exchange plating or etching model [7], which treats the laser heated surface as a thermo-battery and includes simultaneous local plating during the etching process. Nowak et al. [9] and von Gutfeld [15] have shown that in dependence of the metal-electrolyte-combination both an etching in the laser beam center while plating in the periphery and vice versa are possible. Which process is dominating depends strongly on the temperature gradient, the type of dissolved particles and their concentrations. The titanium-phosphorus-oxygen phase shown in Fig. 9could be the result of a phosphate conversion coating of the dissolved Ti<sup>2+</sup>-ions with the phosphate-ions. As a result, hardly solvable titanium-phosphate can be formed, according e.g. to:

$$Ti(H_2PO_4)_2 + HPO_4^{2-} + \frac{1}{4}O_2 \to TiPO_4 + 2H_2PO_4^{-} + \frac{1}{2}H_2O$$
 (2)

Moreover, the covering titanium-oxygen phase (see Fig. 9) can be explained by the frequently formed titanium-oxides. In further investigations a more detailed EDX-Measurement can define the exact atomic-% rations and helps to specify the chemical process. Furthermore, the comparative structuring in water and argon ambient media (see Fig. 3 and Fig. 4) has demonstrated that the formed upstanding structures could not be explained by melting phenomena, since these appear in phosphoric acid at laser powers far below any visible surface modification neither in water nor in argon. The deposition of the titaniumphosphate to the mushroom like material accumulation might be the consequence of laser induced flow dynamics. It is assumed that at defined laser-induced temperatures not only a fast material etching and dissolution of Ti<sup>2+</sup>-ions can be initiated but also a strong convective flow dynamic.





Figure 9 indicates that the etched cavity is not just filled up with titanium-phosphate, but it is the result of a dynamic material deposition in the cavity center due to a thermal induced convective flow. This formation dynamic is schematically shown in Fig. 10. It is supposed that first the etching process according to Eq. 1 gives rise to a local Ti<sup>2+-</sup> ion concentration, which is higher in the cavity center because of the convective flow induced by inhomogeneous surface temperature distribution. Subsequently, the titanium-phosphate deposition according to Eq. 2 is accumulated in the cavity center. This formation process can also explain the elevation above the surface normal. With regard to the boiling-related gas bubble formation it also might be that the electrolyte cross-jet as well as the induced convective flow and formation process is distracted, interrupted or even catalyzed by the emerging gas bubbles.

For example, an attached gas bubble can drastically change the flow conditions, chemical concentrations and heat conditions near the cavity and thereby strongly influence the process. Nevertheless, the surface modifications seen in Fig. 5 strongly depend on the laser power due to its direct influence on the temperature. With increasing laser power the structures first grow in height from the hemispherical accumulation up to the mushroom-like modification. They reach their maximum when the flow dynamic destabilizes due to more turbulent flow effects, like film boiling. As seen in Fig. 3 and Fig. 4, it is also likely that at higher laser power (P > 2.2 W) a material melting takes place and thus suppresses the deposition process.





Both the chemical reaction behavior and induced flow dynamic depend significantly on the induced surface temperature. Fig. 6 shows that the appearance of the titanium-phosphate deposition is inverse related to the laser intensity for different focal spot diameter. That means the etching and deposition processes start neither at a specific laser power nor intensity for the different focal diameters. The relationship between diameter and intensity is shown in Fig. 11. The reciprocal focal diameter over the intensities for the starting etching process in green and deposition process in red follow a linear function (linear regression as dashed line).As can be seen for both process characteristics the reciprocal focal diameter increases in good approximation linearly with the intensity. That means, in accordance  $\frac{1}{d_f} = \frac{1}{\kappa T_c} I \; [12]$  with the centertemperature  $T_{c}\xspace$  of a Gaussian beam and constant material properties  $\kappa$ , a specific threshold temperature is required to initiate the chemical etching  $(T_e)$  and deposition  $(T_d)$ . These threshold temperatures  $T_{e/d}\ characterize$  the formation process as long as κ can be assumed constant. A specific value for the temperature cannot be given here, because it depends on an appropriate assumption of the material properties  $\kappa$  and their boundary conditions, which will be detailed shown in future works. However, from the gradient of the linear regression it can calculate the reciprocal coefficient  $1/\kappa T_c$  to 62.5 for the starting etching (cf. Fig 11, green) and  $1/\kappa T_c$  to 100 for the phosphate deposition (cf. Fig 11, red). These values can be interpreted as process coefficients and represent an easy indicator to predict and describe the disturbance-free etching and deposition behavior when knowing only the laser intensity and focal diameter according to  $\kappa T_c = I d_f$ . That means, if the product of laser intensity and focal diameter is below 62.5 no material modification can be induced, whereas for values between 62.5 and 100 a disturbance-free removal takes place. Above a value of 100 a titanium-phosphate deposition occurs. Thereby, a selective use or avoidance of the observed phosphate formation bv laserthermochemical machining can be controlled. This is especially helpful while structuring larger surface areas, as shown in Fig. 7 or in previous works while creating specific surface finishing [6].

#### Conclusions

- 1. Piled up material accumulations in the etched cavity center during laser thermochemical machining consist of different titanium composites. These are titaniumphosphate and titanium-oxygen deposition as identified by EDX-analysis. Their formation characteristics are strongly related to the used laser focal diameter.
- 2. The evolution of the mushroom-like structures cannot be only explained by the exchange plating and etching model. It was motivated that also laser-induced convective flow dynamics have to be considered. This approach explains the observed surface modification by an increase of the Ti<sup>2+</sup>-ion concentration in the cavity center.
- 3. Within the investigated process parameters the laser thermochemical process stability is confined by constant threshold temperatures. The disturbance-free etching or deposition behavior can be predicted from the laser intensity and focal diameter using the reciprocal gradient  $1/(\kappa T_{e/d})$ .

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