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# Surface finish using laser-thermochemical machining

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**Abstract**

The surface integrity of metallic workpieces after laser chemical machining (LCM) is mainly determined by different corrosion mechanisms such as intergranular, pitting, uniform and high temperature corrosion. The corrosive surface attack is the consequence of a subtractive manufacturing process based on chemical etching in an electrolyte media enhanced by laser heating.
By using a scanner-based LCM-setup uniform corrosion can be used for an effective surface smoothing of titanium workpieces. Independent from the initial surface roughness the smoothing can achieve optical quality ($S_a$ < 0.1 µm) and result in polished surface finish with a macroscopic shiny effect taking into account the relevant laser and scanning parameters. Furthermore, ripple-like surface structures are observed with a periodicity close to the laser wavelength and an orientation perpendicular to the polarization of the laser radiation. While scanning multiple times the ripple structures can be continued coherently over a macroscopic large scale to a high periodic reflection grating.
In addition, electron scanning microscopic study of the material and electrolyte specific characteristics is performed. This reveals microstructure-related intergranular corrosion during the laser chemical polishing. At high laser power pitting and high temperature corrosion dominates the chemical removal process that leads to an increased surface roughness and limits the process time.

Keywords: Polishing; Laser micro machining; Surface integrity; Nano structure; Topography

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## 1. Introduction

Titanium and its alloys like Nitinol are increasingly used in chemical and medical applications mainly due to their high corrosion resistance, biocompatibility and shaped memory effect [1]. Therefore, a gentle and selective surface modification [2] as well as micro material processing with smooth surface properties and low thermal impact is required [3]. Industrial used short-pulsed lasers produce often a significant heating of the material with solidified ablation debris and recast layer [4]. This can lead to unwanted changes to the material properties and a rough surface texture.

These negative effects can be avoided in laser induced chemical machining (LCM) by combining the selective laser processing with a high surface quality and gentle material removal of the chemical processing [5]. Thereby, the laser radiation locally heat up the titanium surface in an electrolyte ambient and enhance a chemical reaction by orders of magnitude due to the changed Nernst potential [6]. The titanium loses its natural passivation property [7] and a local material removal takes place. This material removal process goes hand in hand with a corrosive material attack that is highly sensitive to the process parameter and shows typical corrosion mechanisms such as intergranular, pitting, uniform and high temperature corrosion [8].

Investigations on electrolyte-jet based setups have shown on the one hand the machining potential by etching of different material-electrolyte combination using a three-electrode setup to passivate the workpiece [9] and on the other hand the process limits by occurring disturbances from emerging process gas at higher laser power [10]. To further increase the process speed and accuracy as well as to make a uniform surface processing possible, a laser-scanner based setup was developed. In order to ensure the precise and high quality machining it is indispensable to evaluate the influence of the involved process-parameter and their interaction on the material removal characteristic. On the example of titanium in phosphoric acid the surface texture is investigated in a broad power range in dependence of the laser overlap to identify conditions where stable and controllable surface finishes take place. By using suitable process parameter it is possible to structure large scale direct written optical gratings, polish the surface to optical quality, or deposit phosphorus compounds on the surface.

## 2. Methodology

### *2.1. Experimental setup for laser chemical machining*

One of the key challenges in laser chemical processing is to ensure a controllable and disturbing free laser energy deposition on the workpiece, taking into account the propagation throughout liquid etchant environment. Therefore, the workpiece is mounted in an etching chamber, where a 5 molar (28.7 % vol.) phosphoric acid ($H_3PO_4$) is pumped as a cross-jet through a (25 x 2) $mm^2$ cross-section (Fig. 1) with velocity $v_f$ of 2 m/s. This allows on the on hand the use of a laser-scanning system and on the other ensures, as for a coaxial-jet, a fast evacuation of emerging process gases out of the focus area. As laser source the fibre laser JK400 is used. Its $TEM_{00}$ cw-laser radiation of 1080 nm is focused by a telecentric f- theta optic and guided using the scanning system Raylase Superscan III-15 to the surface. Using a telescope, the laser beam diameter and thus the focal spot size is 110 µm.

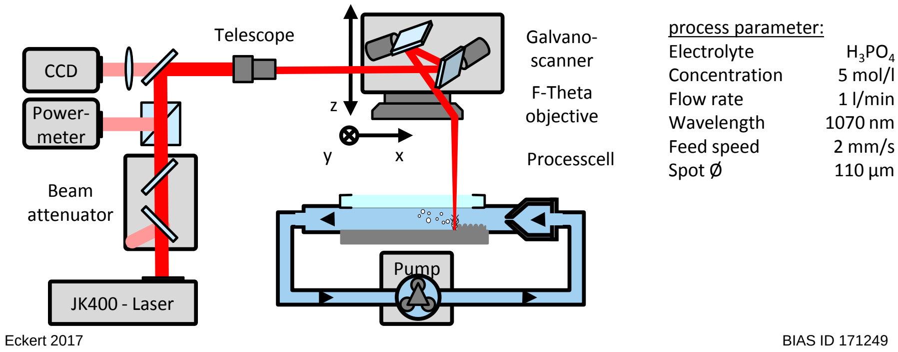


Fig. 1. Schematic illustration of the setup for scanner based selective laser processing in wet-etching environment

### *2.2. Sample preparation and Process parameter*

Rolled titanium (Grade 1) sheets of 0.8 mm thickness are used as sample material. Prior to laser processing the samples are ground with different grain size between P600 and P180 or sand blasted for 2 to 6 s to set a defined initial roughness as summarized in Tab. 1. After grinding, all samples are ultrasonically cleaned for 5 min in isopropanol to remove grinding residues and their roughness Sa is measured with the confocal laser-scanning microscope according to ISO 25178.

Table 1. Summary of sample preparation to set a defined initial roughness

| | Ground | | | | Sand blasted | | | |
|---|---|---|---|---|---|---|---|---|
| Grain size / Time | P1000 | P600 | P320 | P180 | 2 s | 4 s | 6 s | 8 s |
| Roughness Sa [µm] | 0.23±0.03 | 0.33±0.04 | 0.44±0.04 | 0.90±0.08 | 1.02±0.28 | 1.99±0.41 | 2.55±0.56 | 3.78±0.87 |

These samples are structured with single scanning lines hatched for different distances b to arrays of 500 µm x 500 µm with a laser power P from 1.0 W up to 3.5 W. The overlap $U_b$ of these lines differs between 0 to 94 %. The here defined scanning line overlap refers to the width of the focal beam diameter of 110 µm. Since the focal spot diameter, the laser feed speed $v_L$ and electrolyte flow velocity $v_f$ is kept constant at 110 µm, 2 mm/s and 2 m/s, the laser induced surface temperature and thus chemical processes are just determined by the laser power P. The overlap of the single lines is adjusted to create a homogeneous surface processing. While the typical chemical removal rate is between 5 to 10 µm/s, it is necessary to scan the array 5 to 400 times, whereby the repetitions precisely control the surface attack and thereby allow a specific material removal from the surface. Tab. 2 summarized the investigated process parameter.

Table 2. Overview of the varied laser process parameter

| Process parameter | Value / unit |
| --- | --- |
| Roughness Sa | 0.23 – 3.78 µm |
| Laser power P | 1.0 – 3.5 W |
| Line overlap $U_b$ | 0 – 94 % |
| Scan repetition | 5 – 400 |

### *2.3. Methods of surface characterization*

After laser chemical machining the structured surface texture are topographically characterized by using the confocal laser-scanning microscope (Keyence VK-9710). The surface roughness parameter Sa and Rz are optically measured according to ISO 25178. Thus, the surface roughness Sa gives just a bare overview about the surface texture, the gained data are analyzed by determine the roughness in dependence of the spatial wavelength by using a phase-correct Gaussian filter similar to ISO 25178 [11]. The resulting roughness spectrum gives detailed information about the micro- (0.8 – 10 µm), meso- (10 – 80 µm), and macro-roughness (80 – 240 µm) of the surface and how the laser chemical material removal process smooths the roughness peaks. Nano-structural surface features in the range of some 100 nm are investigate using a scanning electron microscope (Zeiss EVO MA10).

## 3. Results

To use the selective laser thermo-chemical induced material removal as a machining process for surface texturing and especially for surface smoothing the influence of the line overlap $U_b$ on the surface roughness is characterized by microscopic images. The laser power P is kept constant at 2.90 W and 50 repetitions, which results in an effective radiation time of 1 s per area unit. The surface roughness against the overlap as well as the initial roughness of 0.3 µm (dashed line) shows Fig. 2 (a).

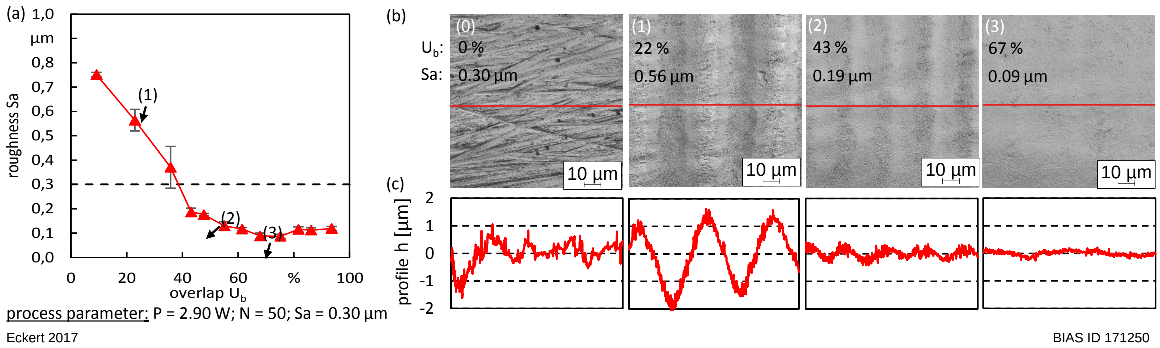


Fig. 2. (a) Laser chemical machined surface roughness Sa over line overlap $U_b$ and their corresponding microscope images (b) with height profile (c)

For overlaps below 40 % the machined surface texture shows an, compared to the unmodified surface, increased roughness up to 0.75 µm. Above 40 % overlap, the surface roughness is on a constant low level around 0.1 µm and reached its minimum of 0.09 µm at 67 %. The microscope images in Fig. 2 (b) shows the unmodified (0) and machined surfaces with 22 % (1), 43 % (2) and 67 % (3) overlap. In the height profile of (1) and (2) the laser scanned lines are clearly visible. They can cause an overall increased roughness despite a reduced noisiness in the height profile (compare (0) and (1)). In the following, an overlap of 67 % is chosen, since it produced the most homogeneous surface texture.

Since the chemical reaction is mainly affected by the temperature [12], the machined surface texture is also highly sensitive to the used laser power as seen in Fig. 3 (a).

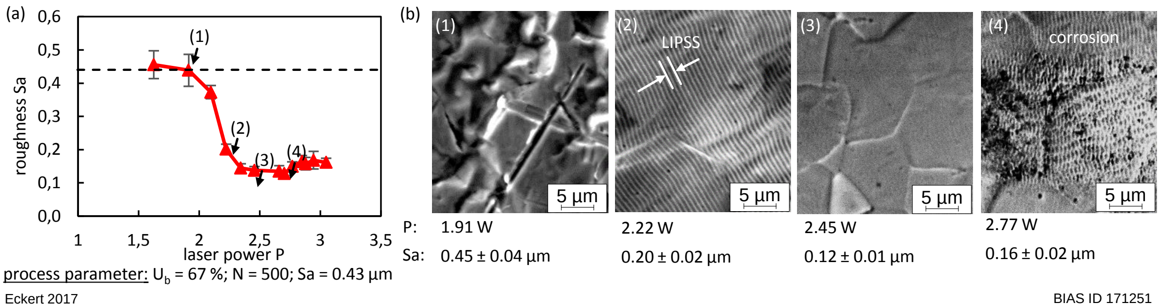


Fig. 3. (a) Laser chemical machined surface roughness Sa over laser power P and corresponding SEM images (b)

The high repetition number N of 500 results in an effective radiation time of 10 s per area unit. Up to a laser power of 2.0 W no roughness reduction (compared to the initial roughness of 0.43 µm - dashed line) or surface modification is observed in the SEM or microscope images (Fig. 3, (b) (1)). Between 2.0 W and 2.2 W the roughness reduce down to 0.2 µm. The laser power of 2.1 W is characterized as modification threshold for the laser induced chemical reaction. The machined surface shows a globular α-titanium microstructure while on the grains clearly high periodic laser induced surface structures (LIPSS) occur (Fig. 3, (b) (2)). The LIPSS form a periodic surface grating which cover the complete machined surface and acts as a reflection grating. The surface texture for higher laser power up to 2.4 W shows clearly the grain boundaries of the globular α-titanium microstructure without any LIPSS (Fig. 3, (c) (2)). At this power the roughness has its minimum of 0.12 µm. A further power increase leads to an increased roughness due to the starting corrosive surface attack by pitting and high temperature corrosion (Fig. 3, (c) (2)). Overall the roughness is still far below the initial value. The sharp drop of the roughness at the modification threshold of 2.1 W is caused by the high repetition number. The low laser power and high repetition number is necessary to produce homogenous LIPSS, since otherwise the LIPSS are not recognizable due to the still high surface roughness. The lower the repetition number, the less the roughness decrease with the laser power. The transition of a rough surface with Sa of 2.71 µm to a smoothed one with 0.19 µm for different repetition numbers of 10, 50 and 300 but constant laser power P of 2.28 W can be seen in Fig. 4, (a).

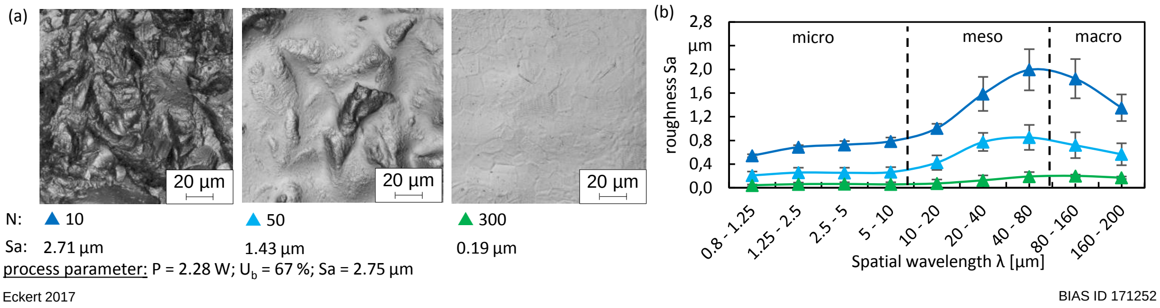


Fig. 4. (a) Microscope images of a laser chemical machined surface and their roughness spectra (b)

Between 10, 50 and 300 repetitions the roughness of the initial sand blasted surface is reduced to 2.71 µm, 1.43 µm and 0.19 µm. It can be seen that the roughness peaks get removed by the chemical etching, while deep cavities still remain on the machined surface. Through further repetitions, these cavities are leveled into the surface one after another. The smoothing mechanism is also investigated in the roughness spectra. The 0.2 s radiated sand blasted surface shows a micro-roughness of nearly 0.7 µm between 0.8 and 10 µm wavelength with a maximum of 2 µm in the meso- and macro-roughness wavelength around 80 µm. After 50 repetitions the whole spectrum is reduced both the micro-roughness to 0.2 µm and the maximum to 0.8 µm. After 300 repetitions, the micro-roughness is reduced further to a roughness of 0.1 µm while the maximum at 80 µm nearly disappears.

The correlation between the number of repetitions and resulting surface roughness is investigated for three different initial roughness of 2.55 µm, 1.70 µm and 0.90 µm at a constant laser power of 2.55 W in Fig. 5.

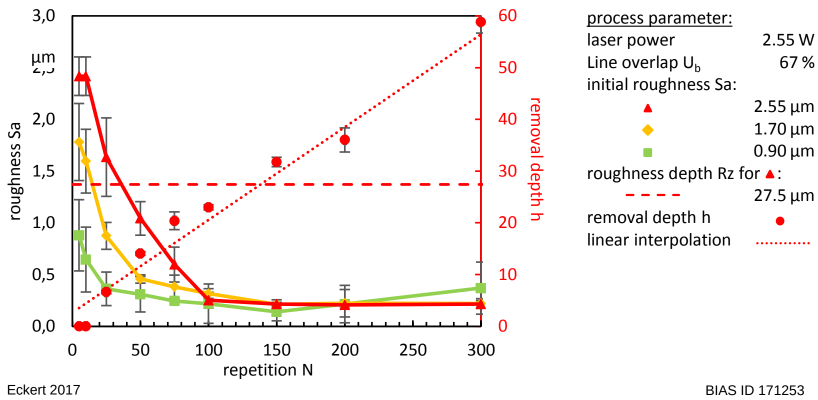


Fig. 5. Correlation between the number of repetitions and surface roughness and the comparison between the removal and roughness depth Rz.

Independent of the initial roughness all machined surfaces achieve (in decreasing Sa order) after 100, 75 and 25 repetitions a similar low Sa plateau of about 0.2 µm. The surface roughness does not significantly improve with further repetitions (comparison of red, orange and green in Fig. 5). Also shown is the material removal depth of the machined surfaces and the roughness depth Rz for the sand blasted surface with the initial roughness of 2.55 µm (Fig. 5, red circles and dashed line). The interpolation suggests an almost linear correlation between the laser chemical removed material and the number of repetitions. After 140 scan repetitions, the removed material exceeds the roughness depth Rz of the initial surface (cross point of the dashed and dotted line).

**4. Discussion**

In the laser thermo-chemical machining the line distance, laser power and scan repetition are of crucial importance for the surface texture. For optimized scan line overlap the hatching influence on the surface waviness can be completely averted. This is possible due to the continuous overlapping of the single Gaussian lines [12]. Despite the process temperature is far below the melting point, it has a strong influence on the surface quality. At high temperatures and thus laser powers disturbing boiling processes starts [10], chemical deposit can occur on the surface [7] and different corrosion processes take place (Fig. 3, (4)). It is assumed that these are mainly caused due to pitting and high temperature corrosion. Also under the optimum laser power of 2.45 W a selective intergranular etching at the grain boundary is observed. This characteristic is process inherent and limits the minimum roughness. In accordance to other works [9] the surface modification by the chemical process starts at a certain threshold laser power (2.1 W) and thus surface temperature. The temperature caused a thermal shift of the Flade-potential, which activate the chemical reaction in the phosphoric acid. Since the chemical material removal rate strongly increased with the laser power, high repetition numbers of 500 are necessary to smooth surface textures near the process threshold. Similar to many other laser ablative processes [14] nearby the process threshold homogeneous LIPSS can be observed. The occurrence of such structures is often discussed in the context of an interaction between the incident laser radiation and excited surface plasmon polaritons. The LIPSS arise perpendicular to the polarization of the laser radiation [15].

The investigation of the surface roughness against the number of repetition for different initial roughness shown in Fig. 4 and Fig. 5 support the idea that the laser chemical smoothing mechanism is based on the selective etching behavior between the roughness peaks and cavities of the surface topology. With increasing repetition it seems that the roughness peaks are attacked faster than the cavities. So that after a few repetitions the surface first gets smoothed in the regime of the micro roughness. While with further repetitions it appears that the surface lowers layer by layer until it is leveled to the depth of the deepest cavity.

This leads to the hypothesis, that the minimal surface roughness is independent of the initial roughness and just determined by the observed corrosive processes. Fig. 5 confirms this, since the different initial surface roughness lead after 100 repetitions within the errors to the same value. Through further scan repetitions there is just a homogeneous material removal without changing the surface texture. The roughness has reached a plateau and cannot be improved any further. This plateau is reached for lower initial roughness with fewer repetitions.

The investigation of the removal depth (Fig. 5, red circle) under consideration of the roughness depth Rz motivates, that the minimum roughness plateau is reached as soon as the removal depth exceeds Rz. Consequently, the roughness depth Rz of the deepest cavity in the surface defines the number of repetition, which are necessary to achieve the plateau. Since the material removal depth increase linearly with repetitions the processing time for smoothing the surface is just defined by roughness depth Rz.

## 5. Conclusion

The experimental results indicate that laser chemical etching can be systematically used for a controlled change of the surface roughness of titanium surfaces. Increasing the surface roughness value goes along with a change of the roughness characteristics, while the reduction of the surface roughness is achieved by a preferred selective chemical attack of the surface roughness peaks, which is independent of the initial roughness level and does not change the roughness characteristics. The removal depth, which is necessary to achieve the minimal roughness, can be predicted from the initial roughness.

To the best knowledge of the author, for the first time the production of direct written laser thermos-chemical induced high periodic surface structures on titanium, which form over a large area a reflective surface grating, was shown. Their occurrence near the chemical material removal threshold is in accordance to similar known structure formation.

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