Removal behavior and output quality for laser chemical machining of tool steels

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Abstract. Laser chemical machining represents a promising technology for manufacturing metallic micro parts. It is usually based on the selective thermal activation of electrochemical material dissolution of self-passivating metals in an electrolyte environment. Prior to widespread industrial acceptance, its machining quality needs to be classified within the subtractive machining processes and the range of machinable materials needs to be expanded. For this purpose, line and square cavities with dimensions ≤300 μm are machined into high speed steel HS10-4-3-10 in a H3PO4-environment and compared to those of the self-passivating cobalt-chrome alloy Stellite 21. As a result, the laser-induced removal velocities in HS10-4-3-10 amount to 50 m m/s. These are two orders of magnitudes higher than the background etching (2 nm/s at room temperature) and three times higher than those obtained in Stellite 21 (12 m m/s). However, the microscopic and spectroscopic analyses of both materials reveal a high shape accuracy with edge radii from 10 to 20 μm, a surface roughness down to 0.8 μm and a negligible microstructural impact. Despite lower removal rates and higher surface roughness, laser chemical machining provides higher dimensional accuracy in comparison with micro milling and shows its suitability for micro machining of structures <200 μm.

Keywords: Micro machining / laser chemical machining / passivation / quality / roughness

1 Introduction

Manufacturing of metallic parts by micro forming is a key approach to meet the ever-increasing demand for micro mechanical and micro electrical components, required for, e.g., consumer products or biomedical devices. Forming dies applied to the manufacture of those components usually exhibit geometrical features of several tenths of micrometers with tolerances in the sub-micrometer range [1]. Therefore, the achievable dimensional accuracy as well as the resulting surface roughness represent crucial figures of merit for micro forming processes [2].

Moreover, tool materials for forming processes require appropriate ductility combined with high hardness and wear resistance [3]. These include mono crystals (e.g. sapphire) as well as ceramic materials (e.g. alumina, zirconia, etc.) and cemented carbides (e.g. tungsten or titanium carbide), which are characterized by complex, time- and cost-intensive production procedures. In addition, metallic alloys such as iron-, nickel- and cobalt-based alloys represent widely used alternative materials. However, the manufacture of micro forming tools from the mentioned alloys is still challenging due to additionally occurring size effects in the microscale [4].

Using conventional machining techniques like milling and turning, which are based on mechanical material removal, the hardness of applied tools should significantly exceed that of the machined material. Thereby, the induced thermomechanical loads can induce additional residual stresses and change the micro structure in the surface-near layers. Thus, the chemical inertia as well the stability could be limited [5]. For forming dies exhibiting geometries or features smaller than 1 mm micro milling is widely used, especially in mold manufacturing, due to its high removal rates (some mm3/min) and its excellent surface finish [6]. To ensure high surface quality, fine grained tool steels with dispersed carbides are used. Thus, a mean roughness value Ra of some 10 nm can be realized. Nevertheless, micro milling is limited regarding the dimensional accuracy and the surface finish; especially when tools of ≤0.2 mm in diameter are applied. This can be explained by the incidence of ploughing effects and feed marks [6].

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Alternatively, hard materials can be manufactured using non-conventional machining. Among others this includes laser machining and electrochemical machining (ECM) [7]. Laser machining, based on material ablation, is characterized by an increased machining precision and quality with shorter laser pulses. However, as the removal rate and the processing quality are reciprocal, the economic use of ultrashort pulsed lasers is still inefficient due to the high procurement costs and the low removal rates (typically $10^{-3}$ mm$^3$/min) [8]. Besides that, ECM is characterized by its smooth and low-cost machining. Due to the purely chemical removal the micro structure properties at the workpiece surface remain unaffected. This makes ECM very suitable for the manufacture of temperature sensitive materials such as NiTi-alloys. Nevertheless, in the microscale, the size of achievable structures is limited by the size of the electrode, which itself has to be manufactured in advance [9].

One process that unifies the advantages of laser and electrochemical machining is the laser chemical machining (LCM). Within this process, the laser beam heats up the workpiece, which is immersed in a continuously pumped electrolyte [10]. Depending on the laser parameters, such as the laser power and spot diameter, the induced thermal heating of the workpiece surface can shift the electrochemical potential to the transpassive region, in which the anodic material dissolution is enhanced. This laser-induced chemical dissolution was observed for different self-passivating metals e.g. stainles steel and titanium alloys [11]. In comparison, materials that do not form a passivation layer when immersed in the electrolyte, are assumed to be non-machinable and thereby are not studied systematically.

Within suitable process windows, laser-induced material removal occurs without micro structural changes, significant heat affected zones or recast formation. The removal quality was found to be the main advantage of the LCM process in comparison to the short-pulsed laser machining, which often results in micro-cracks and distortion effects. Due to the small applied laser power densities ($<100$ kW/cm$^2$ for laser focus diameters below 100 $\mu$m), compared to those in the GW/cm$^2$ range for laser ablation processes, phase changes and material melting are avoided in LCM [12]. However, the LCM process is marked by its high sensitivity against small parameter variations due to the limited process window and by the low removal rates (up to $10^{-3}$ mm$^3$/min) [12]. Further, previous works have shown that the surface roughness depends strongly on the applied scan velocity. The areal arithmetic mean roughness $S_a$ at the ground of micro cavities machined with velocities $<20$ $\mu$m/s into the chrome-cobalt alloy Stellite 21 was found to be $>$2 $\mu$m [13,14], whereby at velocities $>1$ mm/s a polishing effect was demonstrated in titanium resulting in Sa-values down to 0.1 $\mu$m [15]. Hence, the combination of low and high feed velocities could increase the surface quality of LCM-machined micro parts.

Pursuing a strategy that comprises roughing and finishing steps, the aim of this work is to investigate the LCM machinability of metallic materials without self-passivation property and to characterize their removal behavior and quality regarding the dimensional accuracy, the surface roughness and the impact on the material’s micro structure. In addition, the LCM machining quality is compared with micro milling as a reference micro machining technique.

The considered machining task, the experimental plan as well as the analysis methods are introduced in Section 2. Section 3 presents in detail the laser chemical removal behavior of the cobalt-chrome alloy Stellite 21 (self-passivating material) and the high speed steel HS10-4-3-10 (non self-passivating material) in a 5 molar $\text{H}_2\text{PO}_4$-environment. First, the influence of the material passivation property within the used electrolyte is investigated based on single line cavities in dependence of laser power and feed velocity. Second, the influence of lateral overlap on the removal and surface quality is determined in dependence of laser power, feed velocity and scan repetitions. Following that, square micro cavities exhibiting side lengths between 100 $\mu$m and 400 $\mu$m and a depth of 60 $\mu$m, representing forming cavities of micro cold forging dies, are machined into both materials. The geometrical features, the surface roughness as well as the micro structural impact — regarding changes in the chemical composition — on the surface-near layers are investigated in both materials. Furthermore, the machining results are discussed in Section 4 with regard to the material passivation behavior and compared with those of micro milling. Finally, Section 5 closes the paper with a conclusion.

2 Methodology

2.1 Machining task

With the aim to characterize the LCM processing quality in tool steels of different passivation behaviors within the applied electrolyte, micro cavities that are of interest for micro cold forging and embossing, were machined. On the surface of eroded samples with a thickness of 5 mm, square micro cavities with side lengths between 100 $\mu$m and 400 $\mu$m and depths of 60 $\mu$m were laser chemically machined. Figure 1 shows the targeted dimensions as well the quality parameters to be investigated. The characterization includes geometrical properties (side length, edge radius and cavity depth), surface roughness and chemical properties.
properties that can indicate possible micro structural impact related to the machining process.

### 2.2 Materials and electrolyte

An aqueous phosphoric acid solution with a concentration of 28.7% (5 mol/l) was used as electrolyte solution. Moreover, the cast chrome-cobalt alloy Stellite 21 from “Deloro Wear Solutions GmbH” and the high speed steel HS10-4-3-10 from “Hoffmann group” were used as sample materials that are widely used in manufacturing micro forming and cutting tools. Stellite 21 with the chemical composition (>60% Co, 27% Cr, 5.5% Mo, 2.5% Ni and 1.5% Fe) has a hardness of 27 HRC to 40 HRC and possesses a self-passivation property within the used electrolyte solution. A thin oxide layer is built up and protects the material from corrosion. In contrast, HS10-4-3-10 (10% Co, 4% Cr, 3.6% Mo, 3.2% C and 9.5% W) has a hardness of 60 HRC to 67 HRC and does not form a self-passivation layer, so that a material dissolution starts immediately within the used electrolyte environment. The background etching velocities of HS10-4-3-10 in a 5 molar phosphoric acid environment were determined in [16] based on measured weight losses following the DIN 50905. While the background etching rate of 2 nm/s was determined at 20°C, the background etching velocity at 60°C amounted to up to 135 nm/s. Due to the limited heating area (some 100 μm²) in LCM, most regions (with temperatures close to 20°C) will not exceed a background etching rate of 2 nm/s.

### 2.3 Experimental investigation

The cw-fiber laser TruFiber 300 (from Trumpf) was applied as a laser source. Its Gaussian laser radiation of 1080 nm is first collimated to a beam diameter of 8 mm and then focussed using a high aperture lens system (focal length of 50 mm). With this system, the focal spot size d_{spot} amounts to 25 μm. The electrolyte, a 5 molar (28.7% vol.) phosphoric acid solution (H₃PO₄), is pumped through a 2 mm wide nozzle that is arranged coaxially to the laser beam with a velocity v_{beam} of 3.14 m/s. The propagation of the laser beam through the electrolyte affects the power density due to an experimentally identified transmission coefficient τ_{E} of 0.45. More details about the setup can be found in [17].

In order to identify the influence of the relevant process parameters on the removal quality, a systematic investigation was performed in both materials. For this purpose, the laser-induced surface temperatures were calculated following a Green-function based thermal modelling in order to reduce the experimental expenditure [18]. The thermal impact was restricted to surface temperatures below 400°C.

Based on the predicted surface temperatures, two lines of 1 mm in length were first machined for each parameter combination depending on laser power and feed velocity. Second, suitable laser and feed parameters were selected to determine the influence of the degree of overlap O\% or the lateral hatching d_{overlap}, respectively. These quantities depend on the width of single removal line w_{rem} and can be defined as follows:

\[
O\% = \left(1 - \frac{d_{\text{overlap}}}{w_{\text{rem}}} \right) \times 100. \tag{1}
\]

Following, the square micro cavities were machined with a strategy that is similar to that used in micro milling. As a first step, a roughing is applied to achieve the aimed removal depth. In a following step, laser chemical finishing is applied to improve the surface quality. It has to be mentioned that a bidirectional scanning with a 90°-rotation after every scan repetition has been applied. Finally three cavities of dimensions (150 × 150 × 60) μm³ and (300 × 300 × 60) μm³ were manufactured from the two materials in order to be characterized regarding their manufacturing quality and to identify possible influences related to the material passivation behavior. Table 1 illustrates the main parameter variation investigated within this work.

### 2.4 Determination of manufacturing quality

To examine the material-dependent manufacturing quality geometrical properties such as removal depth d_{rem}, edge radius r_{e} and shape accuracy were recorded and characterized using a laser scanning confocal microscope (VHX970-KEYENCE) and a scanning electron microscope (SEM, EVO M10-Zeiss).

In order to enable the comparison with other subtractive machining processes such as electrochemical machining (ECM) the removal velocity v_{rem} was determined as follows:

\[
v_{\text{rem}} = \frac{d_{\text{rem}}}{v_{\text{rem}}}. \tag{2}
\]

For the determination of the edge radius, a 2D holistic approximation was used [19]. Based on an algorithm that uses continuous transitions and an automatic separation of the composite geometries, measured points of a 2D profile line (cross section of the cavity) are assigned dynamically to the individual control geometries (line-circle-line) [20]. The approximation minimizes the orthogonal point

| Table 1. Varied process parameters for the laser chemical manufacture of Stellite 21 and HS10-4-3-10. |
|---------------------------------------------------------------|
| **Parameter** | **Unit** | **LCM** |
| Laser spot d_{spot} | μm | 25 | 25 |
| Laser power P_{L} × τ_{E} | W | 0.4...18 | 0.3...0.6 |
| Peak temperature T_{(x0)} | °C | 100...400 | 100...200 |
| Feed velocity v_{feed} | μm/s | 5...100 | 50...1000 |
| Scan repetitions n_{scan} | – | 1, 2 | 10, 20, 30 |
| Degree of overlap O\% | % | 0...90 | 0...90 |
| Lateral hatching d_{overlap} | μm | var. | var. |
distances to these standard geometries according to the L2-
norm and iteratively improves the parameters of the
composite profiles to fit the measured profile [21]. In this
work, the mean upper edge radius $r_e$ of each cavity was
determined by approximating 20 profile lines spread over
the cavity, half horizontally and half vertically aligned. The
profile lines, for which the holistic approximation did not
converge, due to e.g. excessive burrs along the edges, were
removed from consideration for determining the mean edge
radius. In addition, the removal width and depth of the
removal cavities were evaluated based on automated
Matlab routine, that determines the mean values as well
the standard deviations of minimum 300 cross-sectional
profiles [22]. Further, the areal surface roughness $S_a$ and
the peak roughness $S_z$ were determined at the cavity
ground following the ISO 25178.

To identify the influence of the manufacturing method
on the micro structure, the SEM-records were in addition
complemented by an energy dispersive spectroscoptic
(EDS) analysis to show the chemical composition on
selected regions within the cavities.

3 Results

3.1 Laser chemical removal behavior

3.1.1 Single line removal cavities

3.1.1.1 Removal in Stellite 21

Figure 2 shows the microscopic images of the removal
cavities in Stellite 21 in dependence of the laser power $P_L\times \tau_E$ and feed velocity $v_{\text{feed}}$.

The quantitative characterization of the resulting
removal width $w_{\text{rem}}$ and depth $d_{\text{rem}}$ in Stellite 21 is illustrated in Figure 3. Within the disturbance-free
removal regime (for laser powers between 0.6 W and
0.8 W) it is observed that the removal width $w_{\text{rem}}$ increases
nearly linearly from 17 $\mu$m to 40 $\mu$m with the laser power.
In comparison to the laser power, the influence of the feed
velocity on the removal width is smaller. Moreover, the
removal depth $d_{\text{rem}}$ increases linearly with the laser power.
Once removal disturbances occur (laser powers between
0.8 W and 0.9 W), a clear drop in removal depth is
observed. As discussed in [18], the occurrence of removal
disturbances is caused by the adherence of boiling-related
gas bubbles. Moreover, the removal depth decreases with
rising feed velocity.

3.1.1.2 Removal in HS10-4-3-10

As Figure 4 shows, the resulting removal width $w_{\text{rem}}$ and depth $d_{\text{rem}}$ increased linearly with the laser power.
However, their rise declined with increasing feed velocity.
Between 0.4 W and 2 W, the depth \(d_{\text{rem}}\) increased from around 20 \(\mu\)m to 155 \(\mu\)m with \(v_{\text{feed}} = 5 \ \text{m} / \text{s}\), while only to 60 \(\mu\)m with \(v_{\text{feed}} = 20 \ \text{m} / \text{s}\). At \((P_L \times t_E)/C2 = 0.9 \ \text{W}\) the width \(w_{\text{rem}}\) decreased from 42 \(\mu\)m at \(v_{\text{feed}} = 10 \ \text{m} / \text{s}\) to 29 \(\mu\)m at \(v_{\text{feed}} = 50 \ \text{m} / \text{s}\).

### 3.1.2 Influence of lateral overlapping in large-area removal

For an efficient large-area material removal, the suitable lateral overlapping has been determined based on removal width \(w_{\text{rem}}\) of a single line cavity. Figure 5 summarizes the influence of lateral overlap from 0% to 90% on the cross-sectional profile in Stellite 21 and HS10-4-3-10. The applied laser powers were 0.6 W for Stellite 21 and 0.8 W for HS10-4-3-10, while the scan velocity of 10 \(\text{m} / \text{s}\) were selected for both materials.

In Stellite 21, the waviness at the cavity ground was reduced with increased lateral overlapping. The best results concerning flatness and homogeneous removal were obtained at a lateral overlap of 75%. A further increase up to 90% results in a W-like cross-sectional profile, which is characterized by an intensified material removal at the cavity borders. In contrast, HS10-4-3-10 shows a different behavior. Due to the background etching, a homogeneous removal with low waviness was obtained at a 0% degree of overlap. The flatness of the cavity ground was reduced when decreasing the lateral hatching \(d_{\text{overlap}}\). Considering the conditions of a disturbance-free removal, it was observed that the targeted cavity depth of 60 \(\mu\)m can be achieved with a single scan in HS10-4-3-10, while 2 scan repetitions are required in Stellite 21.

Moreover, the measured surface roughness values \(S_a\) and \(S_z\), shown in Figure 6, revealed that a further improvement of the surface quality is necessary. The arithmetical mean roughness \(S_a\) was found to lay between 1.4 \(\mu\)m and 2.2 \(\mu\)m in Stellite 21 and between 1.2 \(\mu\)m and 3.7 \(\mu\)m in HS10-4-3-10. In contrast, the maximum height \(S_z\) ranged from 15 \(\mu\)m to 35 \(\mu\)m in both materials.

### 3.1.3 Laser chemical finishing

To improve the surface quality on the ground of the cavities, a finishing step was applied. This was based on low laser powers \((P_L \times t_E)/C2 \leq 0.5 \ \text{W}\) and increased feed velocities \((v_{\text{feed}} \geq 50 \ \text{m} / \text{s})\). The energy input per time unit within this parameter range could not result in a detectable removal after a single scan. An additional removal \((>1 \ \mu\text{m})\) is only obtained after several scan repetitions. For that reason, the lateral overlapping during the finishing was varied by assuming a removal width of 25 \(\mu\)m (equal to the laser spot size) for all combinations. The finishing step was performed on roughened cavities that were characterized by an average \(S_a\)-value of 1.9 \(\mu\)m and 1.5 \(\mu\)m and an average \(S_z\)-value of 18 \(\mu\)m and 15 \(\mu\)m in Stellite 21 and HS10-4-3-10, respectively.

Figure 7 shows the influence of laser power, feed velocity and number of scans on the surface quality of Stellite 21. A significant reduction of the surface roughness is obtained with \(n_{\text{scan}} > 20\). The arithmetical mean roughness \(S_a\) was reduced from 1.9 \(\mu\)m down to 1.0 \(\mu\)m. In contrast, the peak roughness was increased with almost all parameter combinations from 13 \(\mu\)m in average to
values ranging between 17 μm and 25 μm. However, with the combination of \( n_{\text{scan}} = 30, P_L \times \tau_E = 0.3 \) W and \( v_{\text{feed}} = 50 \) μm/s, the maximum height \( S_z \) was reduced to 8 μm. In comparison to Stellite 21, the LCM finishing in HS10-4-3-10 was not successful, as the surface roughness was increased to values \( > 2 \) μm for \( S_a \) and \( > 20 \) μm for \( S_z \). Moreover, an additional removal depth of \( < 20 \) μm has been measured.

### 3.2 Manufacturing of square cavities in Stellite 21

#### 3.2.1 Machining strategy

Table 2 summarizes the selected processing parameters for the manufacture of the square cavities in Stellite 21. The cavities were machined based first on a roughing step to achieve the target removal depth and second on a finishing step with the aim to improve the surface quality.

#### 3.2.2 Geometrical properties

Figure 8 shows exemplarily SEM images of laser chemically roughened and finished micro cavities with the targeted dimensions of (300 × 300 × 60) μm³. The LCM roughing results in grossly achieving the cavity dimensions, while the LCM finishing provides a final contouring and a surface smoothing, especially at the cavity ground.

In general, laser chemical machining shows sharp and accurate contours. The visual impressions from Figure 8 were investigated quantitatively by determining the removal depth \( d_{\text{rem}} \) as well as the edge radius \( r_e \), as depicted in Figure 9a. The required depth of 60 μm was already achieved after the LCM roughing. The LCM finishing step led to an additional removal depth of about 12 μm. Thus, the depth of the resulting cavities ranged between 75 μm and 78 μm, while the depth standard deviation was less than 10 μm (see Fig. 9a). Using the 2D holistic approximation (see Sect. 2.4) the mean edge radii (see Fig. 9a) were determined to be 11.21 μm and 18.9 μm for the cavities with side lengths of 150 μm and 300 μm, respectively. Thereby, the \( r_e \)-uncertainties were lower than 1.6 μm. Moreover, the LCM finishing process did not significantly increase the edge radius for both cavity sizes.

Figure 9b shows the surface quality of LCM roughened and finished cavities, which is characteristic for both cavity dimensions, in comparison to the surface of base material. The related arithmetical mean areal roughness \( S_a \) on the cavity ground revealed that LCM roughing is characterized by \( S_a > 1.8 \) μm. This has been clearly reduced during the finishing step down to 0.8 μm. However, the microscopic images (see Fig. 9b) show that the laser-induced waviness has not been totally removed.
3.2.3 Microstructural impact

To examine possible thermal impacts of laser chemical machining on the surface-near layers, the chemical composition at different regions from the ground, the walls and the upper borders of selected cavities were analyzed by energy dispersive spectroscopy (EDS) and were compared with the base material. The mean values obtained from all measurements are illustrated in Table 3. Thereby a dependence of the element distribution on the machining process is observed. Co and Mo showed an inverse behavior. This is clearly visible in particular during the laser chemical roughing, in which on the one hand Co was reduced from 61.2% down to 49% and on the other hand the amount of Mo was tripled to 10.7%. In addition, the laser chemical finishing results in resetting the surface conditions of the base material and removing residues of phosphor and oxygen detected after the roughing step. Additional microscopic images of metallographic cross-sections could not reveal any micro structural changes in the surface-near layers [17].

### Table 3. Mean values of the atomic mass% of the element distribution determined from the EDS-analysis.

|          | Base material | After LCM roughing | After LCM finishing |
|----------|---------------|--------------------|---------------------|
| Co       | 61.2          | 48.7               | 59.1                |
| Cr       | 28.0          | 28.0               | 28.7                |
| Mo       | 3.6           | 10.7               | 3.2                 |
| Si       | 1.3           | 1.4                | 1.0                 |
| O        | 2.2           | 5.0                | 3.2                 |
| P        | 0.0           | 2.1                | 0.1                 |

3.3 Manufacturing of square cavities in HS10-4-3-10

3.3.1 Geometrical properties

As described in Section 3.3, the surface quality could not be further improved within the finishing step. Instead of a surface polishing, the arithmetical mean roughness $S_a$ increased to $>2.3 \mu m$. For this reason, the square cavities in HS10-4-3-10 were manufactured with a single scan repetition using the roughing parameters $P_L \times \tau_E = 1 W$ and $v_{feed} = 20 \mu m/s$.

Figure 10 shows SEM-images of the machined cavities and their related quality parameters. The machining time was kept to a minimum by applying a single repetition with a lateral overlapping of 0% taking into account the permanent background etching. This led to machining times of 37.5 s and 150 s for the manufacture of cavities with side lengths of 150 $\mu m$ and 300 $\mu m$, respectively. The cavity characterization has shown that on the one hand the removal depth amounted to $55 \mu m$ in average. The maximum standard deviations of $3.3 \mu m$ revealed a flat removal in the cavity ground. On the other hand, the mean edge radii ranged between 16 $\mu m$ and 20 $\mu m$ and were similar to those measured in Stellite 21. Moreover, the surface quality obtained ($S_a = 1.5 \mu m$ and $S_z = 14 \mu m$) is typical for the LCM roughing, as low feed velocities ($v_{feed} < 50 \mu m/s$) were applied. In addition, an intensified grain boundary attack was observed due to the unequal dissolution rates of the different phases in the used electrolyte solution.

3.3.2 Microstructural impact

As Figure 11 shows, the chemical composition of the workpiece surface in air (base material) was similar to that in phosphoric acid environment (background etching). Only a presence of phosphor is observed during the
HS-10-4-3-10 in 5 molar H₃PO₄, showed a different removal passivation property within the used electrolyte, such as the hydrodynamic conditions at the interaction zone [22].

Their occurrence depends on the one hand on the material electrolyte boiling point and the beginning of disturbances occur at temperatures ranging between the boiling. As was demonstrated in [18], removal disturbances occur at temperatures ranging between the electrolyte boiling point and the beginning of film boiling. Their occurrence depends on the one hand on the material tendency to build up gas bubbles and on the other hand on the hydrodynamic conditions at the interaction zone [22].

In comparison, the LCM of materials without self-passivation property within the used electrolyte, such as HS-10-4-3-10 in 5 molar H₃PO₄, showed a different removal behavior. The removal depth increases linearly with the laser power and does not show a maximum, as is observed during LCM of self-passivating materials. This can be traced back to the permanent background etching that provides a continuous removal after the laser beam passes the interaction zone and thereby removes possible occurring disturbances.

Concerning the manufacturing of the square cavities, it has been shown that a single scan repetition was sufficient to nearly achieve the required 60 μm in HS10-4-3-10 due to the higher removal rate. However, the surface quality obtained after the roughing step (Sa = 1.5 μm and Sz = 14 μm) could not be improved with a subsequent finishing. In the contrary, the surface roughness has been worsened (Sa > 2.2 μm and Sz > 25 μm).

Concerning the manufacturing, the etching rates over the used material is usually required in laser chemical machining. The LCM of Stellite 21 in phosphoric acid environment shows, as expected, similar behavior compared with other self-passivating materials, such as titanium [23], memory shape alloys (e.g. nickel-titanium alloys) [12] and stainless steel [24]. A detectable (d_{van} > 0.5 μm) and disturbance-free removal took place within some 100 mW (between 0.55 W and 0.8 W). This corresponds to induced surface temperatures below the electrolyte film boiling. As was demonstrated in [18], removal disturbances occur at temperatures ranging between the electrolyte boiling point and the beginning of film boiling. Their occurrence depends on the one hand on the material tendency to build up gas bubbles and on the other hand on the hydrodynamic conditions at the interaction zone [22].

In comparison, the LCM of materials without self-passivation property within the used electrolyte, such as HS-10-4-3-10 in 5 molar H₃PO₄, showed a different removal behavior. The removal depth increases linearly with the laser power and does not show a maximum, as is observed during LCM of self-passivating materials. This can be traced back to the permanent background etching that provides a continuous removal after the laser beam passes the interaction zone and thereby removes possible occurring disturbances.

As demonstrated in [16], the etching rates over the workpiece, expect the limited laser-heated areas (some 100 μm²) will not exceed the background etching rate of 2 nm/s. In comparison, the laser-induced removal velocities (within the interaction area) amounted to 50 μm/s (3 mm/min), which means up to three orders of magnitude higher removal rates than the background etching. Moreover, these velocities are about three times higher than those obtained in Stellite 21, which amounted only up to 12 μm/s (0.72 mm/min) (see Fig. 12).

Concerning the manufacturing of the square cavities, it has been shown that a single scan repetition was sufficient to nearly achieve the required 60 μm in HS10-4-3-10 due to the higher removal rate. However, the surface quality obtained after the roughing step (Sa = 1.5 μm and Sz = 14 μm) could not be improved with a subsequent finishing. In the contrary, the surface roughness has been worsened (Sa > 2.2 μm and Sz > 25 μm). As the EDX-analysis in Figure 11 shows, this can be traced back to the phase-dependent removal velocities as well as to an intensified grain boundary attack.

In contrast, the manufacturing strategy, consisting of roughing and finishing steps, was successfully demonstrated for the LCM of Stellite 21 in phosphoric acid solution. An enhanced material removal, which is characterized by a poor surface quality, was realized with slow scan velocities (roughing step). Besides, controllable and low removal rates have been realized with increased scan velocities and reduced laser powers. This combination was applied during the ensuing finishing step and led to an improved surface quality. The arithmetical mean roughness Sa was reduced from >1.8 μm down to 0.7 μm, while the maximum height Sd from 45 μm was decreased down to 8 μm. However, surface features with spatial wavelengths >10 μm could not be efficiently removed (see Fig. 9b). Considering the micro roughness (spatial wavelengths <5 μm), the results in [15] showed that laser chemical machining is able to achieve values down to 0.2 μm. The LCM-induced surface irregularities are related to two different effects. The first
one is due to the used Gaussian laser beam profile, which results in an inhomogeneous removal even with closed hatching distance [25]. The second effect is related to the unequal chemical dissolution rates of the different elements/phases with respect to the used electrolyte solution [26] as well as the dependence of the achievable surface quality on the micro structure (grain size and element distribution) [15]. Furthermore, it has to be mentioned that the finishing step results also in removing the residues of oxygen and phosphor as well resetting the chemical composition of the base material.

Moreover, the determined edge radii ranged from 16 μm to 21 μm in HS10-4-3-10, while ranging between 10.5 μm and 18 μm in Stellite 21. The slightly higher $r_e$-values in HS10-4-3-10 can be traced back on the one hand to the background etching, which result in smoothing the cavity edges. On the other hand, the decreasing edge radius with increased cavity dimensions (18 μm for the smaller and 10 μm for the bigger cavity size) can be explained by an increased efficiency in transporting the reaction products and exchanging fresh reactants with increased cavity size.

### 4.2.2 Benchmarking with micro milling

The machining quality of laser chemical machining has been compared in detail with micro milling in [17], where the same cavity dimensions, as depicted in Figure 1, were manufactured by micro milling in Stellite 21 using hard coated tungsten carbide ball-end mills with diameters of 0.2 mm and 0.1 mm. The micro milled cavities have undergone the same characterization as the laser chemically machined ones.

Figure 13 shows SEM-images of square cavities (side length of 150 μm) manufactured with both processes. It is seen that the required sharp contours of the square geometry could not be realized with micro milling. The achieved edge radii $r_e$ were larger than those obtained with LCM due to their dependence on the diameter of the applied tool (lower $r_e$-limit was 50 μm as the end ball mill has a diameter of 100 μm). The burr formation in the cavity walls, as seen in Figure 13, could be traced back on the one hand to a local undershooting of the minimum uncut chip thickness and on other hand to a ploughing of the cutting edge in the workpiece. In addition, it was found that the micro milled cavities were subject to an increased presence of oxygen. This indicated that thermal loads were applied to the workpiece due to the friction between the flank faces of the cutting edges and the workpiece material. These effects were possibly intensified with ongoing wear of the flank faces [30]. However, a negative impact on the surface near work piece material layer, such as crack induction, was not determined after the machining experiments.

In comparison, the square shape of the LCM manufactured cavities was sharper and more accurate than that of the micro milled one. This revealed that laser chemical machining (consisting of roughing and finishing steps) is more suitable for manufacturing cavities with dimensions <200 μm due to higher shape accuracy with stable mean edge radii of (11.2 ± 1.3) μm, as can be seen in Figure 13. However, the finish quality of micro milling with arithmetical mean roughness $Sa$ of 0.2 μm could not be achieved with laser chemical machining. Due to in-process induced waviness (at spatial wavelengths between 20 μm and 100 μm), the surface quality could be only improved from $Sa > 2 \mu m$ down to 0.7 μm. Further, the metallographic analysis of the surface-near layers reveals that both manufacturing processes ensure gentle machining without any noticeable micro structural impact.

In view of machining time, micro milling is more efficient than laser chemical machining, e.g., 5 min and 200 min were needed for the machining of one cavity of $(300 \times 300 \times 60) \mu m^3$, using micro milling and LCM.
respectively. However, when considering the tool interaction area \( (31.5 \times 10^3 \mu \text{m}^2 \text{ for the 100 } \mu \text{m ball-end mill and } 2 \times 10^3 \mu \text{m}^2 \text{ for the laser beam}) \), which is about 16 times larger for micro milling, the LCM removal rates were close to those of micro milling. With regard to the tool area, the average removal rates within the applied machining conditions amounted to \( 2.7 \times 10^{-5} \text{ mm}^3/\text{min} \) for LCM and \( 6.75 \times 10^{-5} \text{ mm}^3/\text{min} \) for micro milling.

Looking at Table 4, which summarizes the main benchmarking results between laser chemical machining and micro milling, it can be ascertained that laser chemical machining offers higher accessibility and accuracy in the dimension range of \(<200 \mu \text{m}\). Moreover, LCM offers the opportunity to use one single tool, the laser beam, that can be varied in its properties (spot size, intensity profile and cw/pulsed mode) much easier compared to micro milling, which necessitates a tool change within the process. Nevertheless, it is still challenging to minimize the waviness effect during the roughing procedure. In contrast, micro milling is predestined for the machining of structures with dimensions \( >500 \mu \text{m} \). Further, it is still providing the better surface finish as well as the more homogeneous material removal. Therefore, a combination of both methods to avoid burr formation and to realize better wall curvature is an approach to follow towards the manufacturing of highly accurate micro metallic parts. In view of micro forming processes, a promising application is the high-precision manufacturing of metallic dies, used for micro deep drawing or micro stamping. Here, micro milling can be used for a rough clearing of the die geometry and a high-finish of the ground surface. Subsequently, LCM can be applied for a precise contouring of the die edges. This additional finishing step includes the clearing of possible burr formed during micro milling and the sharpening of the edge radii.

5 Conclusions

The laser chemical machining (LCM) of tool steels was investigated in dependence of their passivation property within a 5 molar phosphoric acid environment. For the self-passivating Cobalt-Chrome alloy Stellite 21 the removal velocities achieved \( 12 \mu \text{m/s} \). Based on the machining strategy, consisting of roughing and finishing steps, the surface roughness \( \text{Sa} \) could be reduced from \( >0.7 \mu \text{m} \) down to \( 0.8 \mu \text{m} \). In contrast, the LCM in the non-passivating high-speed steel HS10-4-3-10 was realized with up to \( 50 \mu \text{m/s} \), considering background etching rates of up to \( 2 \text{ nm/s} \) at room temperature.

Despite the different removal behaviors, LCM of tool steels provides high shape and dimensional accuracy. In this contribution, sharp edge contours with mean edge radii ranging between \( 10 \mu \text{m} \) and \( 20 \mu \text{m} \) were achieved. In comparison with micro milling, LCM is particularly suited for the manufacture of micro cavities with dimensions \(<200 \mu \text{m}\). However, the induced surface waviness presents a limiting factor that affects the surface quality. To further improve the process competitiveness, future works should focus on developing suitable scan strategies to reduce both the surface waviness and roughness.

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### Table 4. Summary of the quality characteristics of laser chemical machining in comparison with micro milling [17].

|                                | Laser chemical machining | Micro milling |
|--------------------------------|--------------------------|--------------|
| Tool diameter [\( \mu \text{m}\)] | 25                       | 100, 200     |
| Cavity geometry [-]            |                          |              |
| Mean edge radius [\( \mu \text{m}\)] | 11...18                 | 25...45      |
| Mean roughness [\( \mu \text{m}\)] | >0.7                     | >0.12        |
| Machining time* [min]          | 200                      | 5            |
| Mean removal rate [\( \text{mm}^3/\text{min}\)] | \( 6.75 \times 10^{-5} \) | \( 1.1 \times 10^{-5} \) |
| Microstructural impact [-]     | Non-significant          | Non-significant |

* For cavity dimensions of \((300 \times 300 \times 60) \mu \text{m}^3\).

** Considering equal interaction areas (similar to those of LCM).
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