

## Influence of electrolyte concentration on laser chemical machining

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### Abstract

To meet the increasing trend of miniaturization, new (non-conventional) manufacturing processes are constantly being developed. The laser chemical process describes one of these non-conventional removal processes in the microscale, based on the thermochemical dissolution of metals. To determine the influence of electrolyte concentrations, linear cavities were created in Titanium Grade 1 using phosphoric acid and sulfuric acid with different concentrations. The experimental results show that as the electrolyte concentration increases, the process window is reduced. One possibility for this is, as the electrolyte concentration increases, the viscosity increases, as well. With increasing viscosity, the electrolyte boiling process, which causes the shielding effect of the gas bubbles becomes more significant. Due to the increasing conductivity of the electrolyte at higher concentrations, the laser chemical removal rate increases within the process window at constant laser power. The maximum removal rate is observed at the maximum conductivity of the electrolyte.

**Keywords:** micromachining, shielding effect, boiling

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### 1 Introduction

The laser chemical process is a non-conventional removal process based on the thermo-chemical dissolution of metals. The laser chemical process links the advantages of laser processing with selective energy input and the advantages of electro chemical machining with a gentle removal process [1].

During laser chemical machining, the workpiece is embedded in an etching cell and irradiated with a laser beam. This introduces heat locally into the workpiece. The introduced temperature gradient starts an anodic material dissolution [2]. Within a suitable process window, this enables gentle material removal without a heat-affected zone and without changing the microstructure. This advantage opens up a wide range of applications for laser chemical machining. For example, materials such as Inconel, which is costly to machine using conventional machining methods, can be processed [3]. Furthermore, the laser chemical process allows a selective and specific adjustment of the surface roughness [4].

However, the machining temperature of the laser chemical process is above the boiling point of the electrolyte [2], resulting in an electrolyte boiling process. The resulting boiling bubbles shield the surface, which results in disturbed material removal. This restricts the laser chemical process window and, consequently, the removal rate. To reduce this limitation, the process can be performed at higher process pressures [5]. This reduced electrolyte boiling and enables thereby higher laser chemical removal rates.

Furthermore, an influence of the electrolyte viscosity by the admixture of the additive PEG (polyethylene glycol) could be determined [6]. With increasing admixture of PEG and thus with increased viscosity, a reduction of the process window was observed. In order to investigate the influence of viscosity in more detail, without the addition of an additive, the influence of varying electrolyte concentrations on the process window and the removal rates was investigated in the present work.

## 2 Methods

A cw fiber laser from the company IPG (YLR-AC100) with a wavelength of 1070 nm was used for the experimental investigations. With the help of a beam attenuator built into the beam path, the laser power was controlled in 0.1 W steps. The beam was guided by an optical fiber with a fiber core diameter of 10  $\mu\text{m}$ . The laser beam was collimated by a collimator and then focused by a lens from “Qioptiq” with a focal length of 93 mm. This resulted in a spot diameter of 25  $\mu\text{m}$ .

Based on preliminary investigations, the electrolytes phosphoric acid and sulfuric acid were used [7]. The concentration of Phosphoric acid was varied from 1 mol/L to 10 mol/L in 1 mol/L steps. The concentration of sulfuric acid was varied between 1 mol/L and 5 mol/L also in 1 mol/L steps.

Prior laser chemical machining, the Titanium Grade 1 samples were fabricated to a size of 20 mm x 20 mm x 1 mm and ground to ensure uniform surface roughness. The fabricated samples were embedded in a chemical cell, see Fig. 1, which was flushed with the particular electrolyte. The propagation height was 46 mm, resulting in a transmission of 0.44.

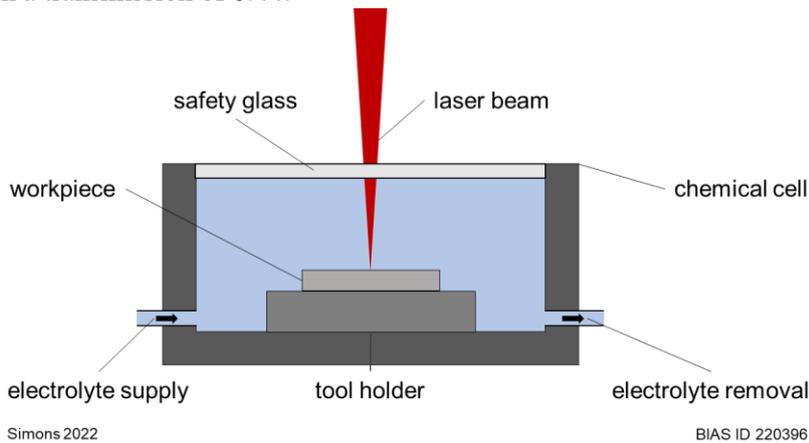


Fig. 1: Schematic depiction of the laser chemical experimental set-up

Linear cavities with a length of 2 mm were fabricated using the set-up described. The evaluation of the fabricated cavities was performed by confocal microscopy. To determine the quality of the laser chemical generated cavities and thus to determine the process window, the respective removal cavities were divided into three categories, depending on the profile of the cavities, according [8]:

Category I (no material removal): No material removal deeper than 0.5  $\mu\text{m}$  is detectable. The laser-induced surface temperatures within the laser chemical interaction zone are lower than the activation temperature at which the passive layer dissolves locally.

Category II (undisturbed material removal): Continuous material removal occurs along the feed direction. This is characterized by a Gaussian profile of the removed material. Within the removal path, there are no material residues or interruptions of the laser chemical material removal. In addition, a lower surface roughness is measurable within the cavity compared to unmachined surfaces.

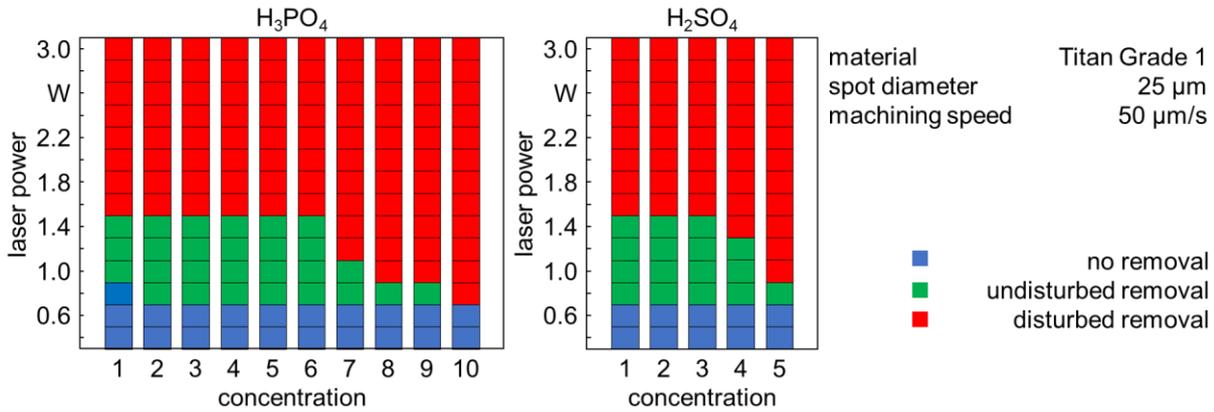
Category III (disturbed material removal): Characterized by deviating non-Gaussian removal characteristics of the surface. Within the cavity, material residues and interruptions of the removal path are visible. In addition, the cross-sectional profile shows a W-shaped material removal. The cavities are characterized by a very uneven and furrowed surface, which is accompanied by a higher surface roughness than category II material removal. In addition, it is noticeable that the width of the generated cavities is several times larger than the width of category II cavities and also larger than the laser spot diameter.

The removal rates were determined analogously to [8].

## 3 Results

Fig. 2 shows the process window for laser chemical machining with phosphoric acid and sulfuric acid at varying electrolyte concentrations. For both electrolytes, it should be noted that the process window becomes smaller at higher electrolyte concentrations. In addition, it should be mentioned that at a concentration of

1 mol/L phosphoric acid and an applied laser power of 0.8 W, in contrast to all other electrolyte concentrations used, no removal could be detected.

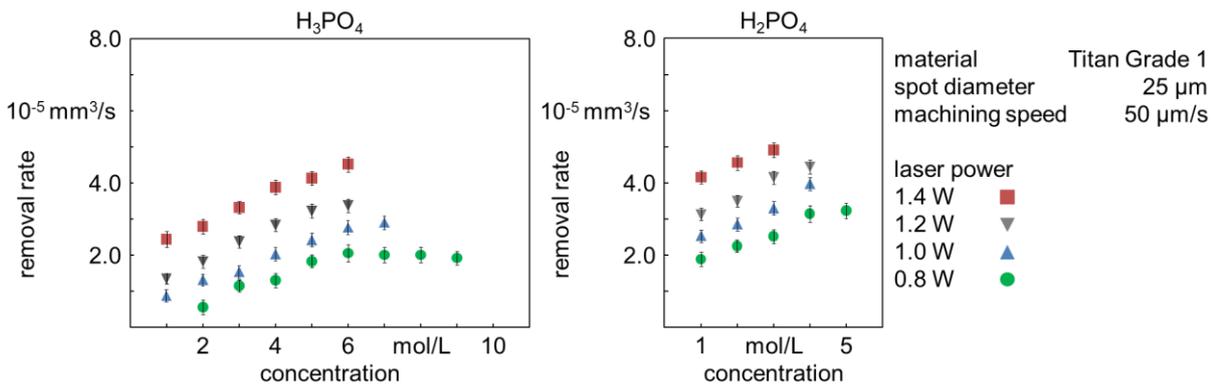


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Fig. 2: Process window of laser chemical machining with phosphoric acid and sulfuric acid

In addition to the process window, Fig. 3 shows the removal rates within the process window (marked green in Fig. 2). It can be seen that the removal rates initially increase. At a concentration of 6 mol/L, the maximum removal rate could be achieved for laser chemical machining of phosphoric acid with constant applied laser power of 0.8 W. For laser chemical machining with sulfuric acid at constant applied laser power, the maximum removal rate was obtained at a laser power of 5 mol/L.



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Fig. 3: Laser chemical removal rates within the process window for laser chemical machining with phosphoric acid and sulfuric acid

#### 4 Discussion

Based on the experimental data, it can be seen that the process window of laser chemical machining reduces at higher electrolyte concentrations, compare Fig. 2. When increasing the electrolyte concentration, there are two opposing mechanisms.

On the one hand, as the electrolyte concentration increases, the boiling points of the electrolytes become elevated [9]. This can be attributed to the fact that increasing the concentration decreases the vapor pressure. Therefore, a higher temperature is required to reach the boiling point [10]. The electrolyte boiling process during laser chemical machining was identified as limiting the laser chemical process window [8]. The gas bubble diameters and the adhesion times of the gas bubbles to the workpiece surface could be determined as critical parameters of the electrolyte boiling process [2]. When the electrolyte boiling temperature is increased, the gas bubble diameters and adhesion times of the gas bubbles to the workpiece surface decrease. This effect could already be observed in [5]. Here, the electrolyte boiling point was increased by increasing the process pressure. As a results, the smaller gas bubble diameters and shorter adhesion times were detected while the applied laser power remained constant. Based on this finding, the laser chemical process window could be extended. However, based on the experimental investigations, it can be stated that no enlargement of the process window takes place at increased viscosities. On the contrary the process window is reduced at higher electrolyte concentrations. Thus, another mechanism predominates over this one.

On the other hand, the viscosities of the electrolytes increase due to an increase in the electrolyte concentration [11]. The increase of the electrolyte viscosity leads to an increased characteristic of the electrolyte boiling process [8]. Due to the increasing gas bubble diameters and adhesion times of the gas bubbles to the workpiece surface, the shielding effect of the gas bubbles comes in effect. This reduces the process window at higher electrolyte viscosities. Based on the reducing process window at higher concentrations of both phosphoric acid and sulfuric acid, it can be observed that this mechanism dominates compared to the increase of the electrolyte boiling temperature.

Considering the removal rates at a constant applied laser power, an increase of the removal rates with increasing electrolyte concentration can be observed at first. Fig. 4 shows the removal rates achieved during laser chemical machining with phosphoric acid and sulfuric acid as well as the conductivities of both electrolytes [12], [13]. It can be seen that with increasing conductivity, the laser chemical removal rate increases. If the conductivity decreases, a decrease in the removal rate can be observed, especially for laser chemical machining with phosphoric acid.

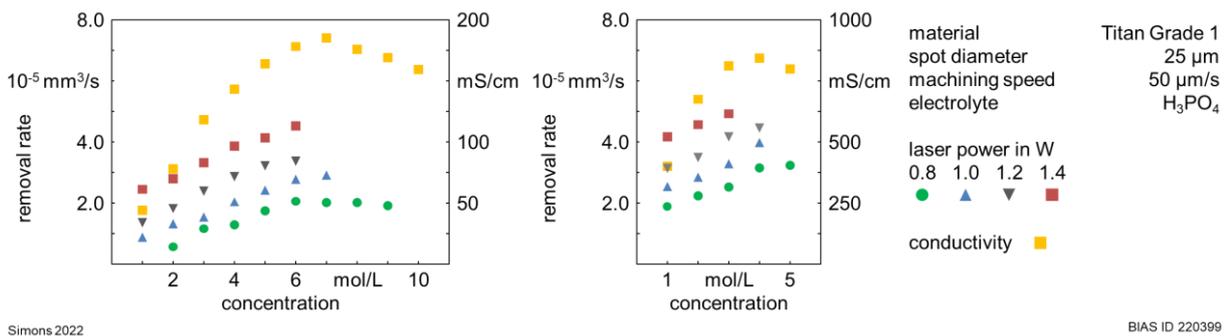


Fig. 4: Laser chemical removal rates and conductivities of the electrolytes phosphoric acid [12] and sulfuric acid [13]

At a concentration of about ca. 7 mol/L and 4 mol/L, respectively, the electrolytes phosphoric acid and sulfuric acid reach the maximum conductivity. Up to these concentrations, an increase in the removal rates during machining with phosphoric acid can be identified. At higher electrolyte concentrations, which do not reach the maximum conductivity a decrease in the removal rates can be observed. Therefore, the removal rate seems to correlate with the conductivity of the electrolyte.

## 5 Conclusion

Based on the present investigations, it can be stated that the dominant mechanism in an increase of the electrolyte concentration regarding the process window limitation during laser chemical machining is the increase of the viscosity in contrast to an increase of the electrolyte boiling point. The maximum removal rate is observed at the maximum conductivity of the electrolyte.

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## References

- [1] Bäuerle, D.: Etching of Metals and Insulators Laser Processing and Chemistry. 4<sup>th</sup> Edition, Springer Verlag (2011)
- [2] Messaoudi, H.: Thermische Bedingungen der laserchemischen Mikrobearbeitung von Metallen. Strahltechnik Band 70, BIAS Verlag: Bremen (2020)
- [3] Simons, M., Beste, L.-H., Radel, T.: Laserchemie Mikrobearbeitung von Inconel 718. Mikroproduktion 10, 3, 26-27 (2021)
- [4] Eckert, S, Vollertsen, F.: Prozessbeschleunigung beim laserchemischen Polieren. Laser Magazin 2, 20-22 (2020).
- [5] Simons, M., Shanta, V., Radel, T., Vollertsen, F.: Bubble behavior during laser chemical machining under superatmospheric pressure. Proc. of the 11<sup>th</sup> CIRP Conference on Photonic Technologies (LANE2020) (2020), eds.: M. Schmidt, F. Vollertsen, E. Govekar. Procedia CIRP 94, Elsevier B.V. Amsterdam (2020), 561-564
- [6] Simons, M., Radel, T.: Laser chemical machining with additive-increased electrolyte viscosity. Proc. 23<sup>rd</sup> Int. Symposium on Laser Precision Microfabrication (LPM2022) (2022)
- [7] Stephen, A., Vollertsen, F.: Mechanisms and processing limits in laser thermochemical machining. CIRP Annals 59, 1 (2010), 251-254

- [8] Mehrafsun, S.: Dynamisches Prozessverhalten bei der laserinduzierten thermochemischen Mikrostrukturierung von Metallen. Strahltechnik Band 67 (2018)
- [9] Peyghambarzadeh, S.M. Hatami, A., Ebrahimi, A., Alavi Fazel, S.A.: Photographic study of bubble departure diameter in saturated pool boiling to electrolyte solutions. Chem. Ind. Chem. Eng. 20, 1, 143-153 (2014)
- [10] anonymous: Properties of Solutions, chemistry LibreTexts, online available: [https://chem.libretexts.org/Bookshelves/Introductory\\_Chemistry/Basics\\_of\\_General\\_Organic\\_and\\_Biological\\_Chemistry\\_\(Ball\\_et\\_al.\)/09%3A\\_Solutions/9.04%3A\\_Properties\\_of\\_Solutions](https://chem.libretexts.org/Bookshelves/Introductory_Chemistry/Basics_of_General_Organic_and_Biological_Chemistry_(Ball_et_al.)/09%3A_Solutions/9.04%3A_Properties_of_Solutions); accessed date: 11.08.2022
- [11] Goldsack, D.E.; Franchetto, R.: The viscosity of concentrated electrolyte solutions. Can. J. Chem. 55, 1062-1072 (1977)
- [12] Machorro, J.J., Olvera, J.C., Larios, A., Hernandez-Hernandez, H.M., Alcantara-Garduno, M.E., Orozco, G.: Electrodialysis of Phosphates in Industrial-Grade Phosphoric Acid. ISRN Electrochemistry, 865727 (2013)
- [13] anonymous: Instrumentation – Acid Concentration, DKL Engineering Inc., online available at: [http://www.sulphuric-acid.com/techmanual/Instrumentation/instr\\_acidconc.htm](http://www.sulphuric-acid.com/techmanual/Instrumentation/instr_acidconc.htm); accessed date: 11.08.2022