Laser-induced liquid-phase jet-chemical etching of metals
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Abstract
In this treatment method laser radiation, which is guided from a co-axially expanding liquid jet-stream, locally initiates on a metal surface a thermochemical etching reaction, which leads to selective material removal. Time-resolved measurements of the electrical potential were correlated with the specific processing parameters to identify conditions for stable and enhanced chemical etching reactions. The chemical etching reaction was additionally influenced by an electrical field. Depending on its polarity a significant increase in the etch rate or improvement of the treatment quality was observed. Exemplary, the fabrication of superelastic micro-grippers prepared by cutting of temperature-sensitive shape memory alloys is shown.

Keywords: Jet-chemical etching; Shape memory alloys; Micro-grippers

1. Introduction
Nowadays, lasers are widely used as a tool for microtechnological treatment of metals with high resolution and quality [1]. Most laser-induced processes for direct micromachining of metals are based on material removal via evaporation by high-intensity pulsed laser irradiation. Consequently, the material is often substantially heated and evaporated by the laser radiation. As a result, redeposition of evaporated or resolidified material can negatively influence the functional properties of laser-produced metallic microparts. Furthermore, in this regime of laser processing thermal damage of the material may occur, thus hindering the application of lasers for localised material removal in high-quality structuring of thermally sensitive materials.

Such problems can be efficiently avoided by using for material removal the process of laser activation of chemical etching reactions at the interface between the solid and a reactive fluid [2]. By the assistance of chemical reactions a much lower surface temperature is necessary in order to activate chemical reactions and removal of material. Laser-induced wet chemical etching of metals can be achieved in different solutions of acids or bases using cw-lasers in the visible or near-infrared region as, e.g., the Nd:YAG laser operating at 1064 nm [3].

2. Experimental
A detailed description of the experimental setup used for laser-induced liquid-phase chemical etching of metals can be found elsewhere [4]. In brief, the beam of a
cw-Nd:YAG laser operating at a wavelength of 1064 nm in its fundamental Gaussian mode at a maximum power of 16 W was focussed to an estimated focal spot diameter of about 20 μm on the metal surface, for instance, superelastic nickel–titanium, which is immersed in a liquid etchant consisting of 5.6 M H₃PO₄ and 1.5 M H₂SO₄. Using a computer-controlled xyz-stage samples were moved under the focussed beam at speeds ranging from 10 to 100 m/s.

To perform laser-induced liquid-phase jet-chemical etching a special liquid-phase etching cell is integrated as shown schematically in Fig. 1. The cell consists of two parts, a co-axial nozzle assembly and a basin, which are connected to each other by elastomer bellows. The nozzle can be adjusted laterally and in height with respect to the laser beam focus. The etch liquid enters the nozzle tip in such a way that a swirl is given the liquid flow and is injected co-axial to the laser beam directly into the irradiated area. Four different nozzle designs with diameters of the tip ranging from 0.5 to 2 mm lead to flow rates of the etchant at the outlet of the nozzle between 2 and 20 m/s. The basin holds the workpiece which is submerged into the etching liquid. The basin is mounted onto computer-controlled xyz-stage allowing a relative movement of the nozzle over a 100 × 100 mm² area at a resolution of 0.1 μm to position the workpiece with respect to the laser beam.

Additionally, a usual three-electrode configuration was integrated into the chemical cell to perform electrochemical enhancement of the reaction. The working electrode is the metallic workpiece itself connected by a silver wire to the potentiometer. The counter-electrode is a circular formed wire made of platinum and is located upside of the workpiece in front of the nozzle. The reference electrode is a standard calomel electrode and located inside the basin.

3. Results

3.1. Process fundamentals

At room temperature many metals are protected against corrosion by a thin native oxide layer on the surface and behave in many aggressive media like a noble metal. So, for example, in phosphoric acid negligible corrosion rates \(<10^{-8} \text{μm/s}\) at room temperature for titanium can be observed [4]. An increase in temperature results in a shift of the chemical equilibrium towards the formation of soluble metal salts and hydrogen.

Time-resolved measurements of the electrical potential against an electrochemical reference electrode show that localised heating of the passivated metal by focussed laser radiation results in analogy to thermal corrosion to a localised dissolution of the passivation layer followed by chemical etching of the metal indicated by a sudden drop of the voltage upon laser illumination as shown in Fig. 2. After the end of laser irradiation a sudden increase in the electrical potential reveals an immediate interruption of the etching reaction due to repassivation of the metal surface which is very essential for a high-quality machining.

In particular, upon laser irradiation a temperature much higher than the boiling point of the liquid can be reached on the metal surface in the zone of laser action. At such high temperatures etch rates several orders of magnitude higher than at the boiling temperature of the etchant were measured. The measured exponential Arrhenius-type dependence of the laser-induced etch rate on laser power also supports the thermal nature of the chemical process [5].

3.2. Laser-assisted jet-chemical etching

In contrast to processing in gaseous media liquid-phase chemical etching benefits from the high density of reactants in the liquid. Since etching processes are transport limited and an increase in metal load of the etchant leads to a decrease in the etch rate a fast exchange of the reaction products with fresh reactants is an essential requirement for avoiding saturation effects of the etch rate.

Such efficient exchange is realised by the liquid jet-stream. It leads to an improvement of the processing speed and treatment quality due to the intensive mass transport and cooling of the workpiece by a direct injection of the etchant into the laser-irradiated area. Fig. 3(a) represents the dependence of the etch rate on the etchant flow rate and
laser power for a nickel–titanium alloy. It shows that etch rates up to 80 000 $\mu$m/s can be achieved for laser powers up to 7 W and a flow rate of 2 m/s. Compared with this, the etch rate at a flow rate of 20 m/s is only half as much. This is due to the higher cooling effect by the liquid jet-stream thus leading to lower thermal activation of the metal and hence to weaker etching reactions. At the same time an enhancement of the etchant flow rate improves the shape fidelity and treatment quality. Thus, an increase in processing speed at equal quality can be achieved by simultaneously increasing the laser power and the flow rate. The microphotographs of machined grooves at three characteristic processing conditions shown in Fig. 3(b) illustrate this effect: no. 3 shows the same high quality as no. 1 at a much higher etch rate which is equal to no. 2 showing a worse quality.

3.3. Laser-assisted jet-electrochemical etching

Due to the ionic nature of the reactants the chemical etching reaction can be additionally influenced by an external electrical field, applied between the metal workpiece and an additional electrode. Laser-induced electrical currents can be observed for a nickel–titanium alloy in the cathodic, active as well as in the passivation region as shown in Fig. 4. The results were obtained by a cathodic scan of the I/U characteristics and pulsing of the laser. In this case, laser-induced currents are due to electrochemical etching reactions caused by thermal activation of the anodic dissolution and/or laser-induced breakthrough of the passivation layer.

The corresponding etch rates are shown in Fig. 5(a) using a laser power of 5 W and a flow rate of 10 m/s. Depending on the polarity of the applied electrical field a significant increase in the etch rate (in the cathodic region) or improvement of the treatment quality (in the passivation region) can be observed as shown in Fig. 5(b). It is assumed that this is caused by an electrochemical reduction of the passive layer towards cathodic potentials enhancing the chemical dissolution.

Thus, combining the influence of three independent process parameters (laser power, etchant flow rate and electrical field) optimum conditions for obtaining predetermined treatment results can be found.

3.4. Cutting of foils

In general, an application for laser-induced jet-chemical etching is cutting of metal foils, for instance, to fabricate microtools of superelastic shape memory alloys for biomedical applications. In this case, it is essential to achieve smooth surfaces inside the cut, nearly perpendicular side walls and to keep the treatment temperature below the transition temperature of the alloy at which the specific properties of the superelastic material get lost.

Grooves can be machined by moving the workpiece perpendicular to the laser beam. Due to the thermal activation of chemical reactions the width and depth of the grooves is determined by the temperature distribution on the surface and the duration of the temperature rise [5]. Therefore, the shape of the groove reflects the intensity distribution of the incident laser beam. In Fig. 6(a) the dependence of the depth of etched grooves in a 200 $\mu$m thick nickel–titanium foil on the laser power is represented at different scanning speeds. In the parameter range investigated an approximately linear dependence of etched depth on laser power is observed.
A groove which was machined using a laser power of 3 W and a moving speed of 10 µm/s is shown in Fig. 6(b). The achieved depth and width is approximately 60 µm corresponding to an aspect ratio of 1. Because of the lateral heat diffusion from the zone of laser action high aspect ratios cannot be realised by single scanning of the groove. The width as well as the depth simultaneously increase with increasing laser power. However, higher aspect ratios can be realised by multiple scanning of the laser beam along the same groove. The groove width is almost independent on the number of scans as the temperature increase is confined to the bottom of the groove. This leads to a continuously increasing depth and, in consequence, to higher aspect ratios. By this method aspect ratios up to 10 have been obtained [6].

As an example of machining microtools by cutting of metallic foils Fig. 7(a) shows a fabricated micro-gripper of superelastic shape memory nickel–titanium alloy and Fig. 7(b) a detailed view on the tip of it as the most important part. The treatment resulted in high machining quality with a roughness $R_a$ of approximately 0.3 µm and cutting angles of $3^\circ$ [7].

Performed bending tests indicate that the superelastic properties are not affected by thermal influences of the process. Thereby, the plastic deformations of the 10 mm long and 100 µm wide gripper arm were measured at the tip of it after applying and releasing again different forces which lead to several increasing bending angles. Fig. 8 represents the dependence of the plastic deformation on the bending angle for different arm width of the micro-gripper. It shows that significant plastic deformations start at $90^\circ$ and continuously increase to 25 µm for $180^\circ$. Indeed, beneath the length the deformation depends strongly on the width. An increase in the width leads to an increased deformation due to the lower aspect ratio which results in higher bending forces, e.g. to a deformation up to 140 µm for a width of 200 µm. However, even for large bends to $180^\circ$ and several repetitions the gripper was still intact and could be bent back.
into its zero position. Additionally, the smooth surface leads to a longer durability, such as bending the micro-gripper several thousand times, since it lowers the susceptibility to micro-cracks which lead to breaking of the material.

4. Conclusion

A precise micromachining process for metals was performed by laser-induced wet-chemical etching. An improvement of machining speed and especially uniformity and reproducibility was achieved by laser-induced jet-chemical etching due to constant flow rates and efficient mass transport. A further improvement of the processing speed and the quality was performed by laser-assisted jet-electrochemical etching.

One application in micromechanics is the fabrication of superelastic micro-grippers generated by cutting of temperature-sensitive shape memory alloys. The achieved angle of the side wall was about 3° and the surface roughness approximately 0.3 µm for machined 200 µm thick foils. Investigations of the mechanical properties showed that the superelasticity of the material is not affected by thermal influences of the process.

The demonstrated machining results showed that laser-induced jet-chemical etching can be applied for the enhancement of the quality of existing products or for enabling the development of new and advanced products.

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References