Localised anodic oxidation of aluminium material using a continuous electrolyte jet

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Abstract. Anodic oxidation of aluminium and its alloys is often used as protection against material wearout and corrosion. Therefore, anodic oxidation of aluminium is applied to produce functional oxide layers. The structure and properties of the oxide layers can be influenced by various factors. These factors include for example the properties of the substrate material, like alloy elements and heat treatment or process parameters, like operating temperature, electric parameters or the type of the used electrolyte. In order to avoid damage to the work-piece surface caused by covering materials in masking applications, to minimize the use of resources and to modify the surface in a targeted manner, the anodic oxidation has to be localised to partial areas. Within this study a proper alternative without preparing the substrate by a mask is investigated for generating locally limited anodic oxidation by using a continuous electrolyte jet. Therefore aluminium material EN AW 7075 is machined by applying a continuous electrolyte jet of oxalic acid. Experiments were carried out by varying process parameters like voltage or processing time. The realised oxide spots on the aluminium surface were investigated by optical microscopy, SEM and EDX line scanning. Furthermore, the dependencies of the oxide layer properties from the process parameters are shown.

1. Introduction
Anodic oxidation of aluminium and many aluminium alloys is well established and most commonly used as prevention against wearout and corrosion. During anodic oxidation, the aluminium substrate material is connected to the anodic potential and immersed into the electrolyte bath. This electrochemical process is used to create a layer of aluminium oxide on the whole surface of the substrate material. The oxide layer grows into the material as well as to the outside and is characterised by its high joint strength with the substrate material.

In order to localise the anodic oxidation to confined sections of the surface, covering materials, such as hoses, plastic foils and insulation tapes, are currently used. These covering materials need to be inert during the anodic oxidation to avoid undercutting. In addition, the covering materials need to be deposited on the material’s surface and removed after the anodisation without damage. Applications of localised anodic oxidation are found on components and component groups, which consist of multiple materials. In these cases the surface characteristics need to be modified sequentially, hence, the anodisation of all sections is technically unnecessary or even damaging. Moreover, in most cases the tribological load, the demand of an adhesive grounding or the decorative
effect is limited to segments of the component. In these cases, the anodisation of the whole immersed component surface is an unnecessary waste of the resource electrical energy. In addition, the localised anodisation offers an approach to the modification of electrical, optical and corrosion-related characteristics.

The application of a continuous electrolyte jet is an adequate alternative for the creation of locally confined oxide spots. Electrochemical machining (ECM) applying a continuous electrolyte jet (Jet-ECM) is a non-conventional technology used to localise the electrochemical machining process at high current densities. So far, it is utilized to remove electrically conductive materials [1, 2]. Figure 1 shows the principle of Jet-ECM.

![Figure 1. Principle of Jet-ECM [2, 3].](image)

The basic principle of electrochemical machining is the anodic dissolution of work-piece material through electric charge transport. The dissolution takes place at the interface between the work-piece surface and the electrolyte, which is a liquid ion conductor. The special characteristic of Jet-ECM is the supply of fresh electrolyte through a micro nozzle at a mean jet velocity of approximately 20 m/s [2, 3].

The electrolyte is ejected perpendicularly towards the work-piece surface in the form of a continuous free jet surrounded by atmospheric air. This leads to a highly localised machining area, because the distribution of the current density is locally confined by the impinging jet.

Extremely high current densities of several hundred A/cm² can be realised [4]. Thus, excellent surface qualities can be machined. In addition, the high jet velocity leads to a very good supply with fresh electrolyte. Hence, there is no need for interrupting the process for flushing phases.

In this paper the application of a free jet for anodic oxidation is investigated. By using an acidic electrolyte the application of this method for the realisation of locally confined oxide spots is analysed.

2. Experimental Setup

For the experimental investigations in localised anodic oxidation, a modular test rig is used [2, 5]. The machine frame in gantry design and the working table are made of granite, which guarantees the required mechanical and thermal stiffness for micro-machining applications.

The electrolyte is delivered by a pulsation-free pump and ejected from the nozzle in Z-direction to the work-piece. Used up electrolyte is collected in a disposal tank. A power supply is used to provide the process voltage up to 300 V. All electrical and kinematic operations are controlled by a personal computer. Therefore, customized control software based on National Instruments LabVIEW was developed [2, 3, 7]. The scheme in Figure 2 illustrates the experimental setup [2, 3].
Figure 2. Scheme of the modular test rig [2, 6].

Figure 3 shows a photograph of the granite table and the processing chamber of the existing test rig.

Figure 3. Photograph of the existing test rig [7].

The relative movement between nozzle and work-piece is carried out by a three-axis positioning system of linear stages. With this setup travel distances of 150 mm in the direction of X and Y and 50 mm in Z-direction are possible. The maximal speed of the linear stages is limited to 5 mm/s by the control software. The nozzle is adapted to the Z-stage, which is mounted to the X-stage. A processing chamber with a lateral dimension of 200 x 200 mm² is adapted to the Y-stage. The work-piece clamping system is integrated into the processing chamber [7].
3. Design of Experiments and Evaluation

The anodic oxidation of aluminium material using a continuous electrolyte jet was investigated by applying oxalic acid on an EN AW-7075 work-piece in peak-aged condition T6. Therefore, localised anodic oxidation without nozzle movement was carried out under variation of processing time and processing voltage. The three-axis setup was applied to realise the infeed movements from one machining point to another.

The experiments were carried out on a work-piece with lateral dimensions of 250 x 200 mm² and a thickness of 3 mm.

In order to remove the natural oxide layer, bating of the work-pieces was carried out before the anodic oxidation process. At first, the work-piece was cleaned with ethanol. Then it was immersed into an aqueous solution with a mass fraction of 10 % NaOH at a temperature between 50 °C and 60 °C for two minutes. Finally, pickling was carried out with nitric acid aqueous solution with a mass fraction of 10 % for another two minutes. The processing parameters for the investigations in localised anodic oxidation are summarised in Table 1.

| Parameter                  | Value                      |
|----------------------------|----------------------------|
| Work-piece material        | AlZn5,5MgCu (EN AW 7075 T6) |
| Electrolyte type , mass fraction | Oxalic acid, 4.3 %        |
| Electrolyte conductivity   | 52 mS/cm                   |
| Electrolyte temperature    | 22°C                       |
| Pump delivery rate         | 10 ml/min                  |
| Nozzle diameter            | 100 µm                     |
| Working gap                | 2500 µm                    |
| Voltage                    | 10 V, 20 V, 40 V, 80 V, 160 V |
| Processing time            | 300 s, 600 s               |

Besides the constant processing parameters given by the work-piece, the electrolyte, the ambient conditions and the setup, the voltage was varied between 10 V to 160 V and the processing time was varied between 300 s and 600 s.

Secondary electron (SE) images were obtained at the sample surface using a scanning electron microscope (SEM) Zeiss Leo 1455 VP. Energy dispersive X-ray spectroscopy (EDX) line scans were conducted across the diameter of anodised spots using an excitation voltage of 5 kV. The oxide thickness was estimated according to the calculated and measured Al/O ratios for different oxide thicknesses on EN AW-7075 alloy in [8].

4. Experimental Results

The results of the experiments in localised anodic oxidation were investigated optically. The oxide spots were arranged with a lateral distance of 4 mm from one another. The experiments with 10 V processing voltage are positioned on the left-hand side of the work-piece. The voltage increases up to 160 V at the right-hand side. In the upper part of the work-piece the experiments with a processing time of 300 s are arranged while in the lower section the same voltages were used at a processing time of 600 s. Figure 4 shows a microscope image of the work-piece surface.
Figure 4. Microscope image of the work-piece with local oxide spots.

From the microscope image it can be recognized that the surface of the work-piece contains a visible change in colour for both of the applied processing times. The circular interference colours represent areas with approximately the same oxide thickness. From the colour gradient within the spots it can be concluded that the oxide thickness varies across the spot diameter. Furthermore, it can be seen that the spot diameter increases with increasing voltage.

In order to detect the content of oxygen and aluminium and to evaluate the oxide thickness on the work-piece surface inside and outside the oxide spots, the work-piece was investigated by SEM and EDX line scanning. Figure 5 and Figure 6 show SEM images of the experiments with processing voltages of 10 V and 160 V after a processing time of 300 s. From the SEM image in Figure 6, it can be derived that the process influences the surface of the work-piece. The machined area shows a dark circle in its centre with a lighter ring around it. At the dark areas on the right side of Figure 6 contaminants on the surface of the work-piece can be seen. In Figure 5, no influence on the work-piece surface was recognized.

Figure 5. SEM image of the area machined at 10 V and 300 s.  
Figure 6. SEM image of the area machined at 160 V and 300 s.

Figure 7 and Figure 8 show the results of EDX line scans. The EDX line scans were captured along the yellow lines highlighted in the SEM images figure 5 and figure 6.
Figure 7 represents the analysis of the oxide spot machined with 10 V and 300 s. It can be seen that the content of oxygen is low in comparison to the aluminium content, which is between 40 counts per second (cps) and 50 cps. Counts per second in EDX analyses are a measurement unit for the quantity of interactions of electrons with the atoms of the displayed element. The resulting absolute values differ in dependence of the measurement parameters, which are defined by the measurement software. Therefore, the ratio between the cps of the single elements is significant for the investigation of the oxide evolution.

Figure 8 shows the analysis of the oxide spot with the parameters 160 V and 300 s. A significant increase of oxygen content can be seen in the middle of the detected line. In this area, the content of aluminium drops from nearly 100 cps to 50 cps while the content of oxygen increases from 20 cps to 50 cps. This can be attributed to an increasing oxide thickness towards the centre of the spot.

Figure 9 and Figure 10 show SEM images of the experiments with voltages of 10 V and 160 V at a processing time of 600 s.

Figure 9. SEM image of the area machined at 10 V and 600 s.

Figure 10. SEM image of the area machined at 160 V and 600 s.
The SEM images show that the work-piece surfaces of both machined areas were influenced by the process. In Figure 9, which shows the experiment with the parameters 10 V and 600 s, a circular area with a dark centre and an increasing brightness to the outside can be recognized. In comparison to the SEM image of the oxide spot in Figure 5, which was machined at shorter processing time of 300 s, the centre has a significantly darker appearance. The SEM image in Figure 10, with the experimental parameters of 160 V and 600 s, shows a dark area in the centre and a significant change in the work-piece surface compared with the SEM image in Figure 6. The differing darkness represents the differing intensity of the interactions of the electrons in SEM imaging caused by differing electric conductivities. From the differing darkness, the hypothesis can be derived, that a larger oxide layer than before was developed. From the comparison of all SEM images, it can be derived that the processing time as well as the voltage have significant influences on the machined areas.

Figure 11 and Figure 12 show the EDX line scans of the SEM images in Figure 9 and Figure 10.

![Graph Figure 11](image)

**Figure 11.** EDX line scan of the area machined at 10 V and 600 s.

![Graph Figure 12](image)

**Figure 12.** EDX line scan of the area machined at 160 V and 600 s.

In Figure 11 it can be seen that the content of oxygen increases slightly to 30 cps in the centre of the detected line while the content of aluminium decreases slightly from 300 cps to 250 cps. Consequently, an oxide layer was developed which is significantly thicker than the oxide layer, which was created after half of the processing time as shown in Figure 7. In the SEM image of Figure 9 a significant influence with a diameter of approximately 500 µm could be detected, but the EDX analysis in Figure 11 hardly represents an amount of oxygen.

In comparison to Figure 11, the content of oxygen in Figure 12 with 500 cps to 600 cps is significantly higher. Furthermore, it can be seen that the content of the aluminium drops from nearly 1000 cps to 500 cps. This indicates that a comparatively thick layer of aluminium oxide was developed during the experiment. In addition, a comparatively wide distribution of oxygen can be derived. Thus, it can be asserted that a higher voltage leads to an increase of the machined area.

Stoichiometric alumina exhibits an O/Al ratio of 1.5. However, slightly higher O/Al ratios may be measured by EDX analysis at the oxide surface due to additional OH-groups. If the excitation depth of the electron beam exceeds the oxide thickness, the EDX measurement will be influenced by the subjacent aluminium alloy. Consequently, the measured O/Al ratio decreases with decreasing oxide thickness.
Figure 13 displays a graph of the oxide thickness as function of the applied voltage. The oxide thickness $d_o$ was estimated from the calculated ratios of the measured O/Al ratios as already published in [8]. The given values represent the maxima of the thicknesses, which are situated in the centre of the machined oxide spots. Maximal thicknesses between 40 nm and 290 nm were realized at a processing time of 300 s while at a processing time of 600 s thicknesses up to 500 nm were achieved. By comparing the two different processing times, it can be seen, that the longer processing time leads to a larger oxide thickness.

![Figure 13. Thickness $d_o$ of the realized oxide spots as function of the applied voltage $U$.](image)

Furthermore, it can be seen, that an increase in oxide thickness is achieved through increasing the processing voltage. In addition, a significantly wider distribution of the local oxide spot was detected at higher voltage. Thus, it can be derived, that the diameter and the thickness of the local oxide spots can be adjusted by adjusting the voltage. The thickness of the local oxide layer can additionally be adjusted by adjusting the processing time.

5. Summary
In this paper an adequate alternative for generating locally confined anodic oxide spots without preparing the substrate by a mask was investigated applying a continuous electrolyte jet. In the experiments a work-piece specimen of EN AW 7075 was machined using oxalic acid. Since aluminium develops a natural oxide layer, bating of the work-piece was carried out before starting the experiments. The machining experiments were carried out at processing voltages between 10 V and 160 V and at processing times of 300 s and 600 s.

The machined areas were investigated optically, by SEM and EDX line scanning. In the optical investigation a colour change of the work-piece surface was recognized. The SEM images showed changes on the surface in the machined areas as well. In both analyses it was asserted, that the voltage as well as the processing time influence the size of the machined areas. The EDX line scanning results showed, that at increasing voltage and processing time the content of oxygen increases and the content of aluminium decreases in the centre of the machined areas. This proves, that oxide layers were developed during the process. Furthermore, it can be seen, that the thickness of the oxide layer increases at increasing voltage and processing time. Local oxide spots with thicknesses between 40 nm and 500 nm were achieved. The diameter and the thickness of the local oxide spots can be adjusted by the voltage and the processing time.
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