Localized anodization of the aluminum alloy EN AW-7075 T6 by closed electrolytic free jet

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Abstract. Anodizing with closed electrolytic free jet enables the resource-efficient, local conversion and surface structuring of the high-strength alloy EN AW-7075 T6 aiming at the local improvement of the tribological behavior of functional surface areas. The objective of the present work was to confine the current distribution on the specimen’s surface and to achieve a stronger localization of the coating oxide layer. For this purpose, the processing parameters working distance, voltage and process duration were varied systematically. Based on the refractive index of the porous oxide and laser scanning microscope imaging of the interference lines, the maximum thicknesses of the anodized spots were calculated. Moreover, the coating microstructure was investigated by scanning electron microscopy and the surface topography was measured with a stylus profiler. The results show that the reduction of the working distance to 100 μm enables a significantly improved localization of the coating growth at substantially lowered process voltages. Thus, the energy-efficient production of localized, wear-resistant oxide spots for tribological applications with local functionalization of surfaces through anodization by closed electrolytic free jet is proven.

1. Introduction
High-strength aluminum alloys are commonly used as lightweight materials for the construction of safety-related structures. However, due to their comparatively low hardness, they are susceptible to abrasive and adhesive wear. The anodic oxidation (anodization) is an established means to overcome this limitation and to open new fields of application [1]. Hard oxide ceramic conversion coatings can be generated in an electrochemical process using an oxalic acid bath at ambient temperature [2]. Conventionally, the whole workpiece is immersed into the electrolyte and connected as the anode. However, in many applications the tribological contact is limited to distinct surface areas, which solely need to be functionalized for wear protection. Hence, the limitation of the anodic oxidation process to highly stressed functional surfaces would allow for saving process energy and prolong the life cycle of the electrolyte reservoir. Furthermore, the dimensional tolerances of surfaces which are not anodized are not affected. Regarding modern light-weight construction, hybrid material concepts gain importance. Those include for example aluminum-polymer compounds or mixed constructions of aluminum and other metals. In this context, anodizing should be limited to the aluminum surface in order to avoid etching of other metals or damaging of polymer surfaces.
In conventional anodization the localization can be realized by masking of surfaces on which an oxidation is not desired with chemically resistant coatings that cannot be subverted by the electrolyte. These coatings have to be applied before and need to be removed after anodization in separate steps. As an alternative, local anodizing can be realized using sealed electrolytic cells. It was proved that micro capillary cells are suitable to generate anodized spots with defined diameters [2, 3]. According to an innovative approach of Kuhn et al., local anodizing can also be performed by using a closed electrolytic free jet [4]. The experimental setup of localized anodization using a continuous electrolytic free jet is extensively described in [4]. The process is closely related to electrochemical machining [5, 6], with the processing parameters such as electrolyte composition and voltage adapted to allow for surface passivation instead of material removal. At the beginning of this process, the surface passivation and coating growth is initiated at the impact area of the jet. With an increase in processing time the diameter of the oxide spot increases significantly since the surrounding surface is also wetted by the electrolyte and the current density distribution expands in lateral direction rather than passing the electrically insulating oxide layer at the center of the anodized spot. Consequently, the spots exhibit a rather low maximum oxide thickness of up to 500 nm in the center and a comparatively large diameter of approximately 2 mm [4].

Although it was proven that the electrolytic free jet technique is suitable to generate anodic oxide spots on high-strength aluminum alloys, localized surface structuring for tribological applications demands for a higher localization of the oxide growth. In order to meet this objective, the distance between the nozzle and the substrate surface was reduced from 2.5 mm to 0.1 mm. The resulting oxide thickness and the diameters of the oxide spots were measured in order to derive their influence on the localization of the coating growth during anodizing of the aluminum alloy EN AW-7075 T6 with closed electrolytic free jet.

2. Materials and methods
Sample sheets of the aluminum alloy AlZn5.5MgCu (EN AW-7075 according to EN 602) with the dimensions of 100 x 25 x 1.5 mm³ were used as substrate material. Grinding with SiC paper down to a grit size of 4000 and subsequent polishing with diamond suspension on polishing cloths were carried out in order to achieve smooth, shiny surfaces prior to anodizing. Due to the mechanical surface pretreatment, there was no necessity for etching prior to anodizing. Thus, the low surface roughness after polishing was not affected. The experimental setup used for anodizing with closed electrolytic free jet was already described in [4]. The used electrolyte was 6.1 g/l oxalic acid, which exhibits a conductivity of 63.1 mS/cm at 21.4 °C and a pH of 1.0. The experiments are conducted in potentiostatic mode at voltages of 20 V, 40 V and 60 V and at a working distance of 0.1 mm. Comparative experiments at voltages of 160 V, 230 V and 300 V and at a working distance of 2.5 mm were carried out to analyze the influence of the increased values. The current flow was recorded as a function of the process time.

In order to evaluate the surface topography, tactile measurements were conducted using a MarSurf LD 120 contour measuring unit (Mahr, Göttingen). An UV-confocal laser scanning microscope (LSM) VK-9700 (Keyence, Neu-Isenburg) was applied to measure the interference patterns at a constant wave length of 408 nm. The maximum thickness of the anodized spots \(d\) was calculated using equation (1) considering the number of the interference lines \(z\) and the refractive index \(n = 1.68\) of the oxide layer, which was obtained from literature [7].

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d = \frac{z \cdot \lambda}{2 \cdot n}
\]

Prior to SEM investigations, the samples were subjected to 3-point-bending with a distance of 40 mm between the bearings up to a maximum deflection of 5 mm in order to generate cracks within the oxide layers. The microstructure was investigated by field emission scanning electron microscope NEON40EsB (FE-SEM, Zeiss,) at selected positions using a tilt angle of 55° to the electron beam.
3. Results and discussion

3.1. Electric current and electrical charge

As already described by Sieber et al., potentiostatic anodizing in closed systems is usually characterized by a current decrease at the beginning due to the passivation of the surface [2]. In case of a compact barrier layer growth, the current can be expected to decrease to almost zero as time passes, because the oxide thickness increases on the entire surface. However, pore initiation and pore growth are typically observed in oxalic acid anodizing. Therefore, the current rises again in the following and eventually, an almost constant current level can be observed during the phase of steady pore growth [2]. As the entire coating thickness increases, a slight current decrease might occur due to the increasing length of the narrow pore channels and the associated increasing diffusion resistance. As can be seen in figure 1, there is only a slight current decrease during the first seconds of anodizing with closed electrolytic free jet, due to the passivation of the surface. No clear current minimum can be observed, because the current flow is not hindered to shift towards outer surface regions with a lower passive layer thickness and therefore a lower electrical resistance. After the initial decrease, the current remains at an almost constant level, which can also be explained by the initiation and growth of pore channels.

![Figure 1. Current-time characteristics of anodizing with closed electrolytic free jet at 40 V and 60 V (work distance 0.1 mm) and 230 V (2.5 mm).](image)

When comparing the current courses displayed in figure 1, it becomes obvious that the reduction of the working distance is a suitable means to achieve comparatively high anodizing currents at significantly reduced process voltages. In this particular case, approximately the same current values could be observed for the process voltages of 40 V and 230 V at working distances of 0.1 mm and 2.5 mm, respectively. Obviously, the electrical resistance of the electrolytic free jet is sharply decreased due to the reduced working distance. Furthermore, it is commonly observed in anodizing that the barrier layer thickness increases proportionally with the anodizing voltage. This effect could also contribute to an increased electrical resistance at high process voltages. However, when increasing the voltage from 40 V to 60 V at a working distance of 0.1 mm, the averaged current also increases by approximately 50%. In this case, the electrical resistance seems to be identical.
3.2. Oxide thickness and microstructure
Provided an almost constant process efficiency, the mass of the anodic oxide is directly proportional to the amount of charge transfer according to Faraday’s law. Since the electric current differs only slightly over the process time, this proportionality also refers to the averaged current. Thus, it can be expected that the highest oxide mass is achieved using a working distance of 0.1 mm and a process voltage of 60 V. Furthermore, the oxide mass directly correlates to the average oxide thickness provided that the specific mass of the anodic oxides considering the density of alumina and the porosity is comparable. With these preconditions, it can be assumed that the average oxide thickness of the spots anodized with a process voltage of 40 V at 0.1 mm of working distance and 230 V at 2.5 mm of working distance are almost equal. Figure 2 represents chosen results of LSM imaging, where the detected interference lines are numbered. The maximum thickness of both anodized spots was calculated according to equation 1). Considering the total number of interference lines of \( z = 16 \) the maximum thickness amounts to approximately 2 \( \mu \)m in both cases.

Figure 2. LSM images of spots with interference lines anodized with a processing time of 20 min at a) a voltage of 40 V and 0.1 mm of working distance and b) a voltage of 230 V and 2.5 mm of working distance

From the similar maximum thickness of both anodized spots a maximal oxide growth rate of approximately 100 nm/min was derived. However, the lateral distribution of the oxide spots varies significantly. While at 230 V the radius of the spot calculated from the second interference maximum to the center, exhibits approximately 750 µm, the radius of the spot anodized at 40 V amounts to only approximately 450 µm in horizontal direction (figure 2 a)). In addition, the circumferential shapes of the oxide spots differ significantly. While an almost rotation-symmetric spot can be recognized at 230 V, the results achieved at 40 V are characterized by an asymmetrical shape with a preferred extraction to the lower part of the image. The asymmetry can be explained by the preferential flow of the electrolyte towards this direction. The process is assisted by additional air flow to displace droplets resulting from the surface tension of the aqueous electrolyte in order to realize the free jet of electrolyte. Since the air flow is characterized by a preferential direction, the electrolyte is preferentially displaced in the same direction, which leads to the asymmetry especially at small working distance. At higher working distance the influence of the assisting air flow is obviously negligible.
A typical oxide microstructure of the anodized spot obtained at 230 V is shown in figure 3. As already derived from the time-dependent current characteristics of anodizing with closed electrolytic free jet in figure 1, the anodic oxide exhibits a porous microstructure. However, pore channels being regularly oriented perpendicularly to the substrate surface are hardly observable in figure 3. Similar highly non-conformal pore structures were already described by Morgenstern et al. regarding the immersion-based anodic oxidation of alloy EN AW-7075 in 0.8 mol/l oxalic acid at a process voltage of 60 V [8]. Moreover, Li et al. observed the growth of highly non-conformal pores during anodizing of high purity aluminum in 0.3 M oxalic acid at process voltages between 140 V and 400 V [9]. This type of competitive pore growth can be assigned to different dissolution rates at the ground of neighboring pore channels [10].

![Figure 3. SEM image of the cracked oxide layer obtained at a working distance of 2.5 mm and a process voltage of 230 V after a processing time of 20 min.](image)

It is known from anodizing in various electrolytes that the diameter of the pore-cells gradually increases with increasing anodizing voltage [11]. For deeper analyses into the applicability of the anodized spots for tribological applications, systematic investigations into influences of the applied voltages on the resulting pore sizes and the resulting hardness parameters are planned for future analyses.

3.3. Surface topography

Apart from the hardness parameters the surface topography is also of great importance regarding both geometrical aspects, e.g. fitting tolerances, and the contact geometry in tribological systems. Typical cross-sectional profiles of anodized spots are presented in figure 4 a). It can be seen that flat elevations result from a large working distance of 2.5 mm. After anodizing with closed electrolytic free jet for 20 min at 230 V, the elevation height amounts to 0.4 µm at an elevation width of approximately 1.5 mm. The reduction of the working distance to 0.1 mm and process voltage to 60 V results in an almost similar elevation width, but at the same time to approximately twice the elevation height. A further reduction in processing voltage to 40 V keeping the working distance at 0.1 mm results in a significant decrease in diameter. Here, an elevation width of approximately 1.0 mm was detected, which represents a reduction to 67 % referring to the comparative results achieved with 60 V and 230 V. At the same time a comparatively large elevation height of 0.6 µm was realized, which is an increase to 150 % referring to the comparative result achieved with 230 V.
Figure 4. Results of tactile measurements: a) cross-sectional profiles of spots anodized with closed electrolytic free jet after an anodizing duration of 20 min and b) development of the maximum profile heights over the process time.

Apart from the topographical information, the time-dependent evolution of the maximum profile height enables us to draw conclusions about the mechanisms of oxide growth. As can be seen from figure 4 b), at the anodizing voltages of 40 V and 60 V, the maximum profile height increases almost proportionally with the anodizing time. Larger profile heights were achieved at a high process voltage of 230 V and a large working distance of 2.5 mm after a short anodizing time of 5 min. This implies a high oxide growth rate in the beginning of the anodizing process. However, the maximum of the analyzed profile height is already achieved after a process time of 5 min, afterwards a declining trend can be observed for increasing anodizing times. Considering the fact that the total oxide thickness increases further to approximately 2 µm after an anodizing time of 20 min as asserted in figure 2 b), this means that the anodic oxide growth proceeds towards the inside of the substrate material. The ratio between outwards and inwards growth rate depends on the ratio of oxide generation and oxide dissolution by the electrolyte.

As the diameter of the anodized spots increases with increasing working distance, the local current density in the center of the spot decreases. Hence, the local oxide growth rate decreases likewise. According to Nagayama and Tamura, the rate of field-assisted dissolution at the pore grounds depends on the local current density and might therefore not contribute to the intensified inwards growth [12]. The authors also state that the chemical dissolution increases with increasing porosity, due to the larger surface of the pore-walls [12]. However, it is not clear from the SEM investigations, whether the coating porosity is affected by the process voltage in anodizing with closed electrolytic free jet. For this reason, further research should be conducted in order to clarify the impact of the process conditions on the oxide porosity and the mechanical properties of the porous oxide layer.

4. Conclusion

The present work investigates the influence of the working distance and the process voltage on the localization of the anodic oxide growth in anodizing with closed electrolytic free jet. The results of optical interferometry show that comparable oxide thicknesses are achieved at considerably reduced process voltage from 230 V to 40 V, when applying a reduced working distance of 0.1 mm instead of 2.5 mm. The results of tactile probing indicate that for anodizing at reduced working distance and voltage an increased elevation height of the oxide spot along with a reduced elevation width is achieved at the same processing time. The reduction in width to 67 % and the increase in height to 150 % results in an increased aspect ratio of 225 %, which is a significant improvement regarding the aspired tribological application.
The results of the SEM investigations show that porous microstructures are generated. Further investigations should be performed in order to gain deeper information about the total porosity and the mechanical and tribological properties of the anodic oxide layers.

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References
[1] Wielage B, Alisch G, Lampke T and Nickel D 2008 Key Eng. Mat. 384 263
[2] Sieber M, Morgenstern R, Kuhn D, Hackert-Oschätzchen M, Schubert A and Lampke T 2017 IOP Conf. Ser.-Mat. Sci. 181 012044
[3] Nickel D, Dietrich D, Morgenstern R, Scharf I, Podlesak H and Lampke T 2016 Adv. Mater. Sci. Eng. 1374897
[4] Kuhn D, Martin A, Eckart C, Sieber, M, Morgenstern R, Hackert-Oschätzchen M, Lampke T and Schubert A 2017 IOP Conf. Ser.-Mat. Sci. 181 012042
[5] Hackert-Oschätzchen M, Meichsner G, Zinecker M, Martin A and Schubert A 2012 Precis. Eng. 36 4 612
[6] Hackert-Oschätzchen M, Martin A, Meichsner G, Zinecker M and Schubert A 2013 Precis. Eng. 37 3 621
[7] Zekovic LD, Urosevic VV and Jovanovic B R 1986 Thin Solid Films 139 109
[8] Morgenstern R, Scharf I and Lampke T 2018 IOP Conf. Ser.-Mat. Sci. 373 012021
[9] Li Y, Ling Z, Hu X, Liu Y and Chang Y 2011 J. Mater. Chem. 21 9661
[10] Chen S, Ling Z, Hu X, Yang H and Li Y 2010 J. Mater. Chem. 20 1794
[11] Lee W, Ji R, Gösele U, Nielsch K 2006 Nat. Mater. 5 741
[12] Nagayama M and Tamura K 1968 Electrochim. Acta 13 1773