Downscaled anodic oxidation process for aluminium in oxalic acid

M Sieber¹, R Morgenstern¹,³, D Kuhn², M Hackert-Oschätzchen², A Schubert² and T Lampke¹

¹Institute of Materials Science and Engineering, Chemnitz University of Technology, 09125 Chemnitz, Germany
²Professorship Micromanufacturing Technology, Chemnitz University of Technology, 09107 Chemnitz, Germany
³corresponding author, email address: roy.morgenstern@mb.tu-chemnitz.de

Abstract. The increasing multi-functionality of parts and assemblies in several fields of engineering demands, amongst others, highly functionalised surfaces. For the different applications, on the one hand, there is a need to scale up surface modification processes originating in the nano- and micro-scale. On the other hand, conventional macro-scale surface refinement methods offer a huge potential for application in the said nano- and micro-scale. The anodic oxidation process, which is established especially for aluminium and its alloys, allows the formation of oxide ceramic layers on the surface. The build-up of an oxide ceramic coating comes along with altered chemical, tribological and electrical surface properties. As a basis for further investigations regarding the use of the anodic oxidation process for micro-scale-manufacturing, the scale effects of oxalic acid anodising on commercially pure aluminium as well as on the AlZn5.5MgCu alloy are addressed in the present work. The focus is on the amount of oxide formed during a potentiostatic process in relation to the exchanged amount of charge. Further, the hardness of the coating as an integral measure to assess the porous oxide structure is approached by nano-indentation technique.

1. Introduction

Service properties of technical products are, amongst others, determined by surface properties. The demand for highly functionalised surfaces arises in all fields of engineering. Not only because of the material and process efficiency, but also because of the trend to miniaturisation of assemblies and products, a scaling-down of conventional manufacturing processes is required. The anodic oxidation process is a suitable means to produce oxide coatings on a plethora of electrically conductive materials, amongst them established light metals like aluminium, magnesium and titanium and also substrates like graphite or silicon. For the latter ones, the formation of very thin, yet functional, e.g. electrically isolating oxide coatings is possible by a strong local anodic polarisation. This polarisation can be realised utilising devices as small as an AFM tip, for instance, and using the ambient humidity as the electrolyte. The application of the polarisation and the associated electric field limits the geometrical extent of the oxidised surface region to the micrometre or even the nanometre range [1-6]. To form functional oxides on metals like aluminium, titanium or magnesium, the ambient humidity is not sufficient because of the low thickness of the oxide layers, which are formed under ambient conditions [7]. Therefore, alkaline or acidic media have to be used, which entails an increased expenditure both with regard to the technical realisation of the process and its costs.
chemical reactions occur during the oxidation of the aluminium and describe the oxide formation (1) and the oxide dissolution in the acidic electrolyte (2):

$$2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- \quad (1)$$

$$\text{Al}_2\text{O}_3 + 6\text{H}^+ \rightarrow 2\text{Al}^{3+} + 3\text{H}_2\text{O} \quad (2)$$

As pointed out in [8], the distribution of the electric field is vital for the formation of a thick oxide layer, since the barrier layer, which is formed at the beginning of the process, impedes the mass transfer and thus further oxide formation. Therefore, a sufficiently high electric field has to be applied to ensure oxide layer growth.

In the present work, scaling effects of the anodic oxidation of aluminium in an oxalic acid electrolyte are investigated in the centimetre, millimetre and micrometre scale. To exclude the influence of inhomogeneous electric field formation, the geometrical extent of the surface modification is limited by restricting the active surface area.

2. Methods and Materials

Two different substrate alloys were used, namely the commercially pure aluminium alloy Al99.5 (EN AW-1050, nominal composition in wt%: Si ≤ 0.25, Fe ≤ 0.4, Cu ≤ 0.05, Mn ≤ 0.05, Mg ≤ 0.05, Zn ≤ 0.07, Ti ≤ 0.05) and the frequently used high-strength alloy AlZn5.5MgCu (EN AW-7075, nominal composition in wt%: Si ≤ 0.4, Fe ≤ 0.5, Cu 1.2–2.0, Mn ≤ 0.3, Mg 2.1–2.9, Cr 0.18–0.28, Zn 5.1–6.1, Ti ≤ 0.2). Both substrates were supplied as sheet metal with a thickness of 1.5 mm and 3 mm for Al99.5 and AlZn5.5MgCu, respectively. Sample pretreatment included etching in 3 wt% NaOH solution (60 °C, 3 min) and in the case of AlZn5.5MgCu pickling in 1:1 diluted nitric acid (room temperature, 30 s). The electrolyte for the anodic oxidation was comprised of 0.8 mol/l oxalic acid (supplied as oxalic acid dehydrate, Merck, Germany). The electrolyte temperature was 25 °C. All the used chemicals were of analytical grade.

The anodic oxidation was carried out with a constant voltage of 60 V for 15 min. Three different scales of the active surface area were considered, namely the centimetre, millimetre and micrometre scale. The power supply for the experiments in the centimetre scale was a pe1028 (Plating Electronic, Germany) and the active surface of the sample was approx. 50 cm². The power supply for the millimetre and micrometre scale was a potentiostat Zahner IM6 with voltage booster CVB120 (Zahner, Germany) and the active surface was approx. 80 mm² and 500 µm², respectively. For both of the power supplies, the values of current and voltage were logged internally during the process with an acquisition rate of 1 sample/s. A saturated Ag/AgCl electrode was used as reference in both the millimetre and the micrometre scale. A platinum sheet and a platinum wire served as the counter electrode in the millimetre and the micrometre scale, respectively. No reference was used in the centimetre scale and lead sheets served as the counter electrode in this case. All potential values acquired in three-electrode-arrangement are given in relation to the standard hydrogen electrode. In the centimetre and the millimetre scale, the electrolyte was constantly stirred, while in the micrometre range, the electrolyte movement was realised via a volume flow through the cell of 4 µl/s. A schematic representation of the different experimental setups for the considered scales is given in figure 1. The coating thickness was determined by light microscopy in the cross sections of the samples. Being a conversion coating process, a part of the coating thickness lies inside of the original substrate dimensions, while the other part lies outside. The relation of these dimensions was considered by partially shielding the substrate by a polyurethane lacquer in the centimetre scale and by the given experimental setup in the other scales. Thus, it was possible to recognise the original substrate surface in the cross section and to determine the parts of the oxide coating, which apparently grew in inward and in outward direction. The hardness of the coatings was obtained from instrumentated indentation tests in the cross sections of the coatings with a Berkovich indenter (Asmec Unat, Germany). A load of 5 mN was applied (load time 10 s, hold time 5 s, unload time 4 s). The indents were placed at different locations in the coatings. Because of the rather low coating thicknesses, the typical decay of
the hardness with increasing distance from the substrate does not occur. Therefore, the mean hardness values are given for the considered coatings.

**Figure 1.** Schematic representation of the experimental setup for the three different scales – a) micrometre scale: a capillary filled with electrolyte is placed on the substrate and the inner capillary diameter defines the active surface area; b) millimetre scale: the sample is placed in a sample holder, which limits the active surface area; c) centimetre scale: the sample is placed in an electrolyte basin, the active surface area is defined by the sample size.

### 3. Results and Discussion

A representative curve for the evolution of the current density over the process time for the potentiostatic regime at 60 V for 15 min is given in figure 2. Initially, the barrier oxide layer formation takes place, which leads to a decrease of the current flow within the first few seconds of the process. The reason for this is the character of the barrier layer, which acts as a resistance against current flow. Afterwards, the formation of the typical pore structure takes place, which is accompanied by an increase of the current density. With the growth of the porous layer, the resistance of the oxide layer increases slightly with the time and therefore the current density slowly decreases in the course of the process. The transferred amount of charge, which is calculated by integration of the current density over the time, is shown in figure 3 for the different substrate alloys and scales. It is obvious, that the amount of charge transferred in the process is significantly lower for the AlZn5.5MgCu alloy compared to the commercially pure aluminium substrate Al99.5. The reason for this behaviour lies in the alloying elements, mainly Zn and Cu, which impede the substrate conversion process and therefore lead to a lower current density and hence charge transfer. Also, it has to be noted that the charge transfer in the centimetre and the millimetre scale is in a similar range, but there is significantly less charge transfer in the micrometre range. Two effects are responsible for this behaviour: For the AlZn5.5MgCu alloy, excessive oxygen evolution occurs during the anodic oxidation. While in the millimetre and the centimetre range, the oxygen can freely flow off through the electrolyte, it reduces the effective cross section of the electrolyte-containing capillary, and therefore impedes the current flow. This leads to a premature end of the process after approximately 700 s due to complete blocking of the surface. Additionally, the electrolyte-containing capillary itself acts as a significant resistance due to its small cross-section so that also for the Al99.5 substrate, for which practically no gas evolution occurs, the charge transfer is significantly lower in the micrometre range. Thus, the influence of the experimental setup is, although undesirable, not negligible in this case.
Figure 2. Representative evolution of the current density over the process time for a potentiostatic anodic oxidation process of Al99.5 at 60 V in 0.8 mol/l oxalic acid at room temperature in the micrometre scale. Qualitatively, the same curve appears for the centimetre and the millimetre scale for both alloys with different absolute values of the current density.

Figure 3. Charge transfer in the potentiostatic anodic oxidation process (60 V in 0.8 mol/l oxalic acid at room temperature, 15 min) for the two different alloys in the considered scales of the active surface area.

Figure 4 shows a representative cross section of an oxide coating with adjacent active and inactive surface areas, which allow the determination of the “inward” and “outward” coating growth. The resulting thickness values of the formed oxide coatings for the considered alloys and scales of the active surface are shown in figure 5. In accordance with the impediment of the anodic oxidation process by the alloying elements and the charge consumed by the evolution of oxygen, the coating thickness formed on AlZn5.5MgCu is generally lower than on Al99.5. Considering the millimetre and the centimetre scale, there is no significant change of the coating thickness. The coating thickness is much lower in the micrometre scale because of the geometrical conditions in the micrometre scale.
setup and, consequently, the effect of the electrolyte resistance. It is noticeable that the relative amount of "inward" coating growth becomes higher with the reduction of the scales. However, no single effect can be made responsible for this behaviour. Except for the experimental setup and the occurring resistances therein, the conditions of the electrolyte flow in the system as well as the temperature distribution within the substrate (local or global temperature rise and relevance of the heated volume compared to the volume of the sample) have to be considered. Further investigation focusing on both abstraction and definition as well as isolation of experimental conditions is necessary to clarify the found behaviour.

An overview of the hardness of the oxide coatings in the cross section is given in figure 6. It is noticeable that the hardness of coatings on the Al99.5 substrate is significantly higher than on the AlZn5.5MgCu substrate, which is caused by a higher density of flaws in the coatings on the alloy. These originate from the disturbance of the aluminium conversion process by the alloying elements, which are either dissolved or incorporated into the oxide. Both of the mentioned processes are accompanied by oxygen evolution and as a result, the regular pore structure of the coatings becomes disturbed and larger flaws arise. This consequently leads to a lower coating hardness in accordance with the literature [9, 10]. There is no significant effect of the scale of the active surface area on the hardness. This inevitably implies that the temperature distribution at the interface substrate/oxide/electrolyte is roughly identical for all the scales, which otherwise would exert an effect on the hardness according to the literature [11]. The hardness of the oxide coatings on AlZn5.5MgCu produced in the micrometre scale is not considered, since the low coating thickness did hardly allow for an appropriate placement of the hardness indents.

![Representative cross section of an oxide coating with adjacent active and inactive surface areas](image)

**Figure 4.** Representative cross section of an oxide coating with adjacent active and inactive surface areas (E – embedding resin, O – oxide coating, S – substrate).
Figure 5. Thickness of the oxide coating formed in the potentiostatic anodic oxidation process (60 V in 0.8 mol/l oxalic acid at room temperature, 15 min) for the two different alloys in the considered scales of the active surface area. The combined height of the boxes represents the coating thickness, the single boxes represent the amount of oxide grown outwards and inwards with reference to the original dimensions of the substrate (0).

Figure 6. Hardness measured in the cross section of the oxide coatings produced on the two different alloys in the different scales of the active surface area.

4. Summary
The effect of different scales of the active surface area on the anodic oxidation of Al99.5 and AlZn5.5MgCu in oxalic acid was considered with regard to the amount of charge transferred during the anodic oxidation, the resulting coating thickness and hardness. The presence of the alloying elements, especially zinc and copper, in the AlZn5.5MgCu alloy impedes the oxide formation reaction and therefore decreases both the charge transfer and the resulting coating thickness in comparison to Al99.5. The hardness in the cross section of the coating is lower for the AlZn5.5MgCu alloy, which is also attributed to the alloying elements, which led to an increased number and size of flaws in the coatings in accordance with the literature. The different scales of the active surface area do not exert an effect on the hardness. The experimental arrangement led to a higher system resistance in the micrometre scale so that the charge transfer and hence the coating thickness were reduced in comparison to the millimetre and the centimetre scale.
Acknowledgments
The authors gratefully acknowledge funding of this work by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG, project LA1274/40-1). The support by Dagobert Spieler, Elke Benedix, Gabriele Tauchmann, Sigrid Kaufmann, Christel Gläser, Karla Muhr and Franz Nozicka (all from the Institute of Materials Science and Engineering) is gratefully acknowledged.

References
[1] Bartosik M, Kolibal M, Cechal J, Mach J and Sikola T 2009 J Nanosci Nanotechnol 9 5887
[2] Hu K, Wang Q and Wangyang P 2013 Int J Nanomanuf 9 496
[3] Kolanek K, Gotszalk T, Zielony M and Grabiec P 2008 Materials Science Poland 26 271
[4] Li Y F, Sugiyama M and Toshiyoshi H 2015 J Microelectromech Syst 24 1471
[5] Mori G, Lazzarino M, Ercolani D, Biasiol G, Sorba L, Heun S and Locatelli A 2005 J Appl Phys 98 114303
[6] Suehisa Y, Aoki T, Shimizu J, Zhou L and Eda H 2009 Key Eng Mater 389-390 424
[7] Davis Z J, Abadal G, Hansen O, Borise X, Barniol N, Perez-Murano F and Boisen A 2003 Ultramicroscopy 97 467
[8] Jee W Y, Kim J G and Chu C N 2015 Int. J. Precis. Eng. Manuf. 16 2623
[9] Runge J M and Hossain T 2015 Mater Today Proc 2 5055
[10] Zhou X, Habazaki H, Shimizu K, Skeldon P, Thompson G E and Wood G C 1996 Corros Sci 38 1563
[11] Aerts T, Jorcin J B, De Graeve I and Terryn H 2010 Electrochim Acta 5 3957