

Anodisation with dynamic current control for tailored alumina coatings

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Abstract. The anodic oxidation process is commonly used to refine the surface of aluminium and its alloys. Compared to the substrate, the alumina layers produced by anodising exhibit an increased hardness and chemical resistance. Thus, the corrosion and wear resistance are generally improved. The coatings are also electrically isolating and may serve decorative purposes. Applying a time-variant, dynamic electrical process control by pulse-current or current-steps is a promising approach to improve the coating properties, which is partially deployed in an industrial scale. In the present work, the influence of dynamic electrical process control on the coating properties is examined by means of a design of experiments (DOE). The effects of various electrolyte compositions and temperatures as well as processing time are considered with regard to coating thickness, hardness, wear resistance and the electrical energy consumption during the formation of the coatings. Information about the statistical significance of the effects of the parameters on the considered properties is obtained by an analysis of variance (ANOVA).



1. Introduction

The surface refinement of aluminium and its alloys by anodic oxidation in sulfuric acid electrolytes generally improves both corrosion and wear resistance. Therefore, the formed oxide-ceramic layers offer the possibility to access a wider range of application for these lightweight materials. However, the anodic oxidation process is rather costly with regard to the required energy, especially electrical energy for the process itself and the cooling of the electrolyte. The latter is necessary to produce harder coatings with a reduced volume of the characteristic pores, which form during the process because of a complex interrelation between oxide formation and the subsequent dissolution of the oxide material in the electrolyte.

Several approaches have been established to improve the energy efficiency of the anodic oxidation process. This includes the use of electrolyte additives [1–4] as well as the optimisation of the electric parameters [5–8]. The application of time-variable voltage- and/or current-regulation to tailor process and coating properties has been investigated [9–13] and discussed controversially [14] by many researchers.

The aim of the present work is to clarify the effect of time-variable electric regimes for the anodic oxidation on the properties of the formed oxide coatings. The influence of pulsed and stepwise variable current regimes is compared to the influence of electrolyte additives, temperature and process time by means of a DOE (design of experiments). Thereby, the total charge transfer quantity is kept constant within the process to allow for the comparison of both coating properties and the necessary amount of electrical energy to produce the coating. To avoid burning of the samples in the later process stages, the voltage is limited to 70 V. For the sake of comparability between direct current and dynamic current control, high mean current densities (above 10 A/dm²) are avoided.

2. Experimental methods

2.1. Coating formation – materials and processing

The aluminium alloy AlMgSi1 (nominal composition 0.7–1.3 % Si, ≤0.5 % Fe, ≤0.1 % Cu, 0.4–1.0 % Mn, 0.6–1.2 % Mg, ≤0.25 % Cr, ≤0.2 % Zn, ≤0.1 % Ti, Al balance) was used as substrate (dimensions: 6 mm x 12.7 mm x 25.4 mm). The pretreatment of the samples included etching in 3 wt-% sodium hydroxide at 50 °C for 1 min and pickling in 30 vol-% nitric acid at room temperature for 30 s followed by rinsing under deionised water.

The electrolyte volume for the anodic oxidation was 2 l. The electrolytes were prepared using deionised water, sulfuric acid (Merck, Germany), glycolic acid (Sigma-Aldrich, Germany) and the commercial electrolyte additive Anodal EE (Clariant, Germany). All chemicals were of analytical grade. Three different electrolyte compositions were used: (A1) 20 vol-% sulfuric acid + 20 g/l glycolic acid; (A2) 20 vol-% sulfuric acid; (A3) 20 vol-% sulfuric acid + 20 ml/l Anodal EE. The electrolyte temperature was maintained at (B1) 5 °C, (B2) 15 °C and (B3) 25 °C with the help of a thermostat. Galvanostatic process control was applied with a pE1028 power source (Plating Electronic, Germany). Three different types of galvanostatic control were used: (C1) direct current; (C2) pulsed current with a pulse width of 2 min at the higher current and 30 s at the lower current, the ratio of the higher to the lower current being 5/1; (C3) stepwise time-variant current with 3 equally spaced steps over the process time

using 2/3, 3/3 and 4/3 of the mean current density. The process time was set at (D1) 30 min, (D2) 45 min and (D3) 120 min resulting in a mean current density of 6.3 A/dm², 4.2 A/dm² and 1.575 A/dm², respectively, to ensure a constant turnover of electric charge in the process. The parameters A–D were varied according to a DOE using a modified Box-Behnken-Design [15] with 25 different combinations of the four parameters. Four samples were produced and tested for every set of parameters. Figure 1 shows a graphical representation of the DOE. After the coating formation process, the specimens were rinsed under water and dried under cool air.

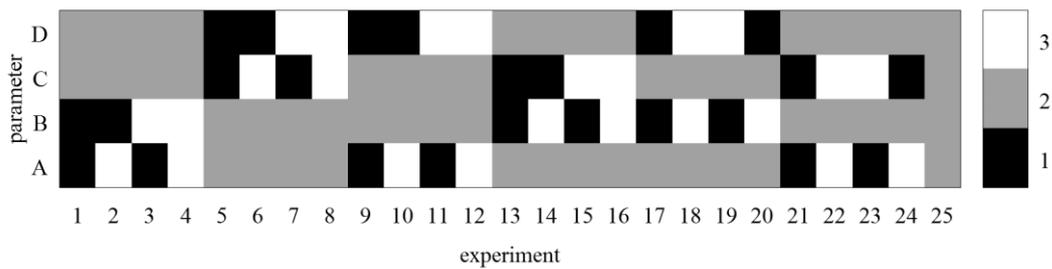


Figure 1. Graphical representation of the DOE used in this work showing the assignment of parameter levels (1–3) to 25 experiments with 4 repetitions, each, with parameters A – electrolyte composition, B – temperature, C – current regime, D – process time.

2.2. Process and coating characterization

During the anodic oxidation process, current and voltage values were logged with a sampling rate of 1 Hz using the internal logging function of the power device. Afterwards, the electrical energy W_{el} used for the process was calculated by integrating the product of current density and voltage depending on the process time.

The coating thickness s and the hardness H were determined in the cross sections of the coatings (Martens hardness HM 0.05/30/30 by Fischerscope HM2000 XYm, Fischer, Germany). It is well known from the literature, that the oxide coatings produced by anodising declines with increasing distance to the substrate. Therefore, the distance of the hardness indents to the substrate/coating interface was determined to assess the gradient of the hardness decline (hardness gradient H' in N/mm³). For each sample, three hardness profiles with five indents were measured.

As an integral property, the scratch energy density w of the coatings was determined. With a Revetest-RST (CSM Instruments, Switzerland), a Rockwell diamond (radius 200 μ m) was scratched across the sample surface with a constant load of 15 N for 5 mm. The scratch energy density w was calculated according to Eq. 1 using the mean tangential force during the scratch test F , the scratch length l and the scratch volume v , which was determined by measuring a linear surface profile (tactile measurement, T4000, Hommelwerke, Germany) normal to the scratch direction at five different positions:

$$w = F \cdot l \cdot v^{-1} \quad (1)$$

2.3. DOE exploitation

For each of the properties W_{el} , s , H' and w , the mean values and the standard deviation for each level of each parameter were determined. All values for the respective property obtained at a specific parameter level were taken into account. For example, the standard deviation of parameter A at level 1 includes all results with varying parameters B, C, D. Further, an error probability p_{err} for considering the parameters as significant with respect to a specific property was obtained by performing an analysis of variance (ANOVA) with the Matlab built-in function “anovan” [16]. The error probability p_{err} characterises the probability of committing an error in considering the effect of a parameter on a specific property as significant. It provides information, whether the results obtained for at least one level of the parameter are statistically significantly different from the results obtained at the other levels.

3. Results and discussion

A typical voltage/current density characteristic during the anodic oxidation process is shown in figure 2 (experiment no. 25, compare figure 1). It is apparent, that the voltage increases with the process time. This behaviour is due to the growing of the oxide layer, which results in an increased electrical resistance. Figure 3 shows the influence of the process parameters on the consumption of electrical energy during the anodic oxidation W_{el} . With the exception of the current regime, every parameter wields a statistically significant influence over W_{el} . The addition of organic components (A1, A3) into the electrolyte as well as the reduction of the temperature attenuate the dissolution of formed oxide material and therefore increase the process voltage and hence W_{el} . The difference between the two used electrolyte additives is insignificant according to the ANOVA, though there is a tendency towards lower W_{el} for the glycolic acid additive compared to the commercial additive. However, the difference to the sulphuric acid electrolyte without additives is significant. Interestingly, the longest process time is attended by the lowest W_{el} value. Obviously, the low current density used in the longer processes involves (1) a low voltage and (2) a reduced voltage increase over time. Hence, the amount of consumed electrical energy decreases. There is no significant difference in W_{el} between 30 min and 45 min process time.

The effect of the parameters on the coating thickness s is shown in figure 4. Although the influences of electrolyte, temperature and process time are rather small, they are statistically significant according to the ANOVA with error probabilities of less than 3 % in any case. Considering the electrolyte composition, the glycolic acid additive increases the mean coating thickness by approximately 10 % while the commercial additive shows no significant effect compared to the sulfuric acid electrolyte without additions. The relatively lower coating thickness in the electrolyte with the commercial additive is caused by the limiting of the voltage at 70 V, which was sometimes the case in electrolyte A3 because of the strong increase of the process voltage caused by the additive. Consequently, the amount of charge transferred in the process decreases and thus the coating thickness is reduced. With regard to the electrolyte temperature, the coating thickness is at the same level for 5 °C and 15 °C. Only an increase to 25 °C causes a reduction of the thickness. However, the current regime does not

wield a significant influence on the coating thickness, which is apparently related to the constant amount of charge transferred in the process. Hence, the same amount of oxide is formed. With reference to the process time, the results for 30 min and 120 min are not statistically significantly different from the results obtained for 45 min, but they are statistically significantly different compared to each other. Therefore, the tendency of a lower coating thickness with increasing process time is small, yet statistically significant. This and the effect of the temperature can be explained with an increased dissolution of formed oxide material because of the longer exposition to the electrolyte with increasing process time and because of the stronger chemical attack on the oxide with increasing temperature.

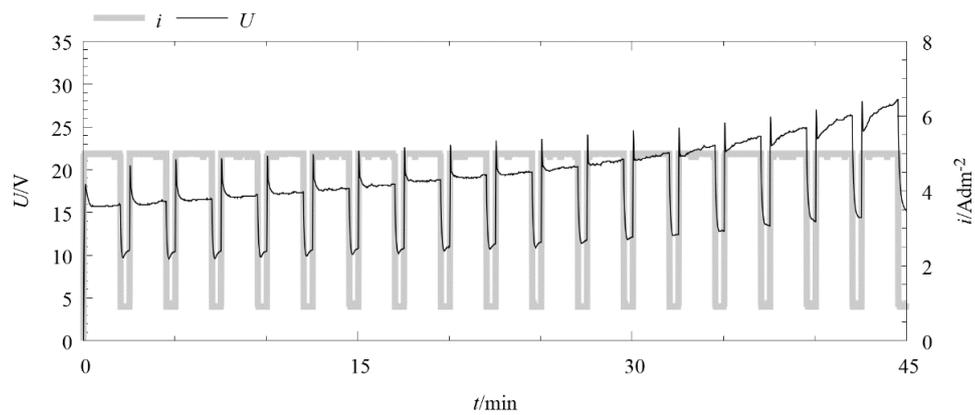


Figure 2. Voltage and current density in dependence of the processing time during experiment no. 25.

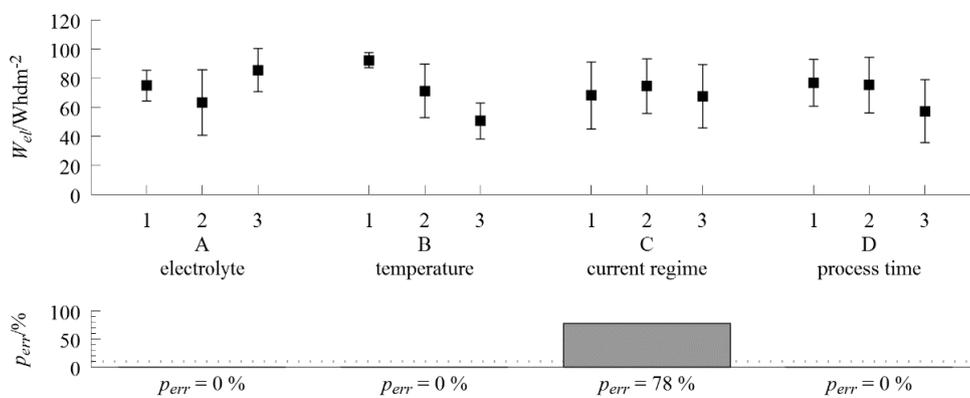


Figure 3. Effect of electrolyte, temperature, current regime and process time on the electric energy consumption during the anodic oxidation and corresponding error probability obtained from the ANOVA.

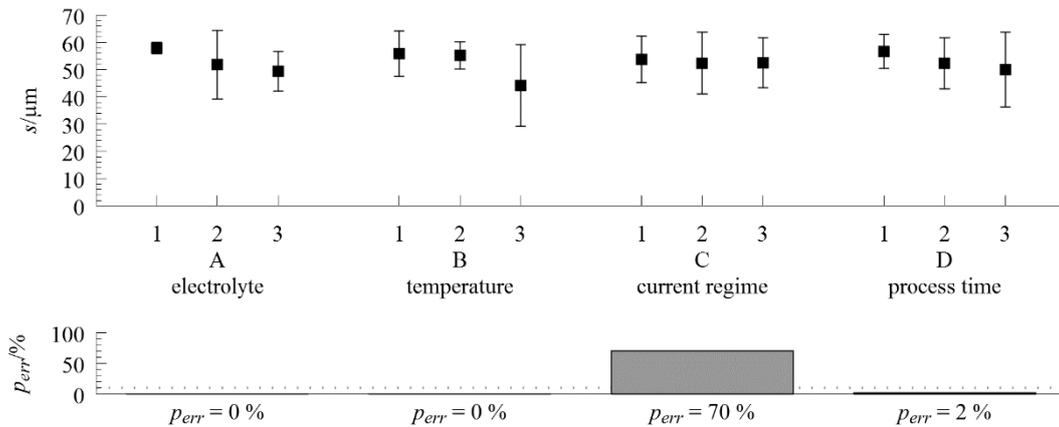


Figure 4. Effect of electrolyte, temperature, current regime and process time on the coating thickness and corresponding error probability obtained from the ANOVA.

With regard to the hardness gradient H' , i.e. the gradient with which the hardness is reduced with increasing distance to the substrate, the temperature and the electrolyte composition are the factors with the biggest influence (figure 5). Reduced chemical dissolution caused by a decreased electrolyte temperature or the addition of both the tested organic components to the electrolyte leads to a less pronounced widening of the pores because of chemical attack on the formed oxide. Thereby, the results for the two electrolyte additives do not differ significantly from each other but the hardness gradient is significantly decreased compared to the sulphuric acid electrolyte without additives according to the ANOVA. The same results are obtained with regard to the electrolyte temperature: there is no significant difference between the hardness gradient of coatings obtained at 15 °C and 5 °C, while the hardness gradient is significantly increased at 25 °C. The correlation between pore volume and hardness has been established in [17]. As for the other properties, the current regime does not exert a statistically significant effect.

The scratch energy density w is strongly dependent of the electrolyte composition and the temperature (figure 6). Interestingly, the mean value of all experiments at an electrolyte temperature of 25 °C (B3) is very small compared to that of the other parameters. This indicates that the variation of neither the electrolyte composition, current regime nor the process duration is suitable to improve the scratch energy density of samples anodized at 25 °C. Both the results obtained for coatings formed at 15 °C and 5 °C show a higher scratch energy density. Thereby, a temperature decrease from 15 °C to 5 °C does not lead to a higher scratch energy density. The influence of the additives on w reflects the results of the hardness gradient measurements. The organic additives significantly improve w compared to the pure sulfuric acid electrolyte. Again, the ANOVA shows that there is no difference between the two electrolyte additives. Process time and current regime do not exert an influence on the scratch energy density according to the analysis of variance.

The use of the dynamic current control in the chosen parameter field does not exert an influence on the tested coating and process properties. Further, in accordance with [18], any improvement with regard to the coating's thickness, hardness or wear resistance is attended by a higher amount of electrical energy required for the process. Nonetheless, there might be conditions, e.g. very high mean current densities or the anodisation of other alloys, which do not allow for a formation in direct current mode and require the use of dynamic current control.

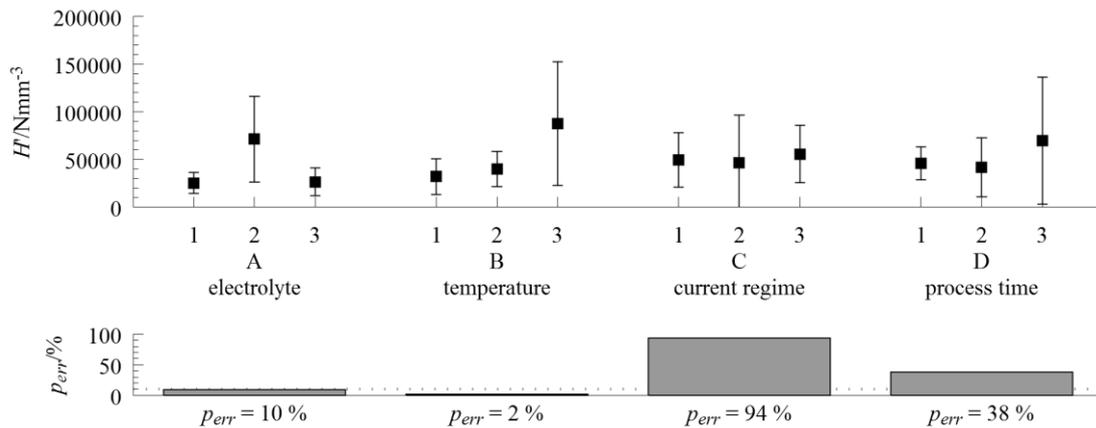


Figure 5. Effect of electrolyte, temperature, current regime and process time on the hardness gradient and corresponding error probability obtained from the ANOVA.

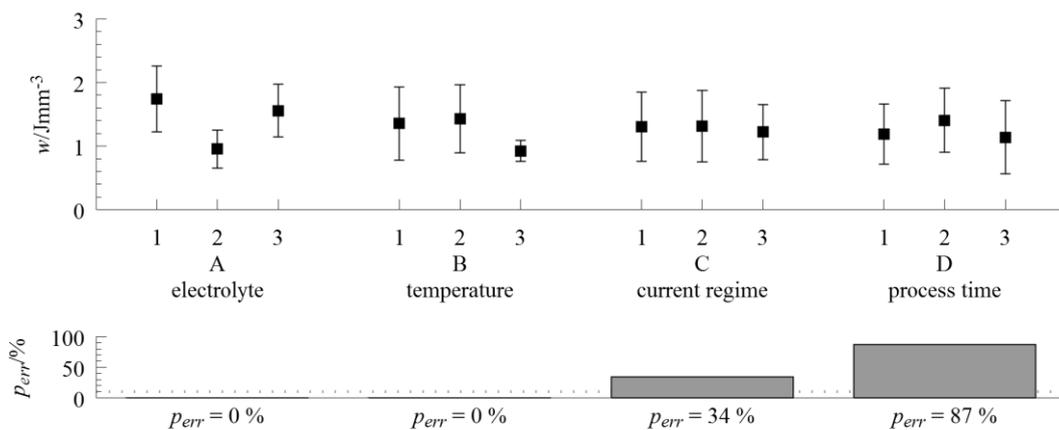


Figure 6. Effect of electrolyte, temperature, current regime and process time on the scratch energy density and corresponding error probability obtained from the ANOVA.

4. Conclusion

The influence of the electrolyte composition, temperature, current regime and process time on selected properties of the anodic oxidation process and the formed oxide layers were investigated. The used three-level DOE was exploited with regard to electric energy consumption during the coating formation, thickness, hardness gradient and scratch energy density of the coatings. Thereby, the amount of charge turnover in the process was kept constant, given that the process voltage did not exceed 70 V. The obtained results can be summed up with regard to the considered parameters as follows. Both the commercial and the non-commercial organic additive generally increased the energy consumption and improved the coating properties. Hardly a difference was found between the two additives. The reduction of the electrolyte temperature generally increased the electrical energy consumption. With regard to the considered coating properties, however, the reduction of the temperature from 15 °C to 5 °C showed no significant improvement. The choice of the current regime (direct current vs. pulse-current vs. current-steps) affected neither the electrical energy consumption nor the coating properties in the considered range of parameters. With regard to the process time, there was no difference in electrical energy consumption and coating properties between 30 min and 45 min. While an increase to 120 min decreased the electrical energy consumption, it also deteriorated the coating properties in terms of thickness and hardness gradient.

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