Corrigendum: Formation of corundum-rich alumina coatings on low-carbon steel by plasma electrolytic oxidation (2021 IOP Conf. Ser.: Mater Sci Eng. 1147 012007)

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The surface area of the test sample depicted in figure 2 was calculated wrong (without the contribution of the lateral area). That’s why the current densities in Table 3, Figure 4 and Figure 5 were wrong also. We adjusted the mentioned article elements as well as the corresponding statement within the abstract:

**Abstract**: As a result of this, it was possible to obtain alumina layers of 80 micrometers in thickness, with a high corundum content of approximately 50 to 90%, after 37 minutes of treatment time, at a current density below 10 (instead of 25) A/dm² on C8C-steel.

**Table 3. Parameters of the symmetric current-controlled alternating rectangular pulse for PEO.**

| $I_1$ / A | $i_1$/A·dm⁻² | $t_1$/ms | $U_1$/V | $I_2$ / A | $i_2$/A·dm⁻² | $t_2$/ms | $U_2$/V |
|-----------|--------------|-----------|---------|-----------|--------------|-----------|---------|
| 1         | 10.85        | 5         | 500     | -0.5      | -5.42        | 5         | -500    |
Figure 4. Graphical representation of the electrical pulse regime at 15 minutes of PEO treatment after initial voltage staircase: process-voltage (a), current-density (b), and photo-voltage (c) along with the associated limits, definitions, and pre-discharge values. These (a-c) are then summarised into a voltage current density-characteristic (d), with photo-voltage indicated by colour, combined with an image of the process.

Figure 5. Course of the process voltage and current-density extremes (a) as well as the maximum and minimum values of the photo-voltage (b) as dependent on the process time.
Formation of corundum-rich alumina coatings on low-carbon steel by plasma electrolytic oxidation

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Abstract. The plasma electrolytic oxidation (PEO) is an innovative method for providing light metals and their alloys with protective ceramic surfaces. However, for iron-based materials, the process requires very high current densities and results in the formation of coatings which consist of less stable iron compounds. Therefore, it was the aim of this study to design a PEO procedure on low-carbon steel at moderate current densities, which allows for the formation of ceramic coatings whose chemical composition is dominated by the electrolyte constituents. The electrolyte used was based on aluminate and preselected by systematic electrochemical passivation experiments. The PEO treatment was monitored by electrical and optical process diagnostics. As a result of this, it was possible to obtain alumina layers of 80 micrometers in thickness, with a high corundum content of approximately 50 to 90%, after 37 minutes of treatment time, at a current density below 25 A/dm² on C8C-steel. However, the coating’s microstructure was inhomogeneous and showed poor substrate bonding. Based on the results of the experimental work, explanatory approaches were provided and a course of action is suggested for counteracting these problems.

1. Introduction
Plasma electrolytic oxidation is an innovative method for the surface treatment of metallic materials. During the process, the workpiece is immersed within an aqueous electrolyte, opposite a counter electrode and receives a strong alternating polarisation. If suitable process parameters are chosen, this procedure leads to the formation of an electrically insulating passive layer on the sample surface. This result in a strong localised voltage drop between the substrate and an area of equal electrical potential, the so-called quasi cathode, close to the substrate/electrolyte interface. Generally, the initiation of the plasma electrolytic discharge occurs during the anodic partial pulse. They strike out of the electrolyte and into the substrate, leading to the formation of a ceramic layer. Depending on the selected process parameters, the PEO coating can be composed of oxides of the substrate material or contain more complex reaction products of the substrate and electrolyte constituents. [1, 2]

While the method was initially developed for the surface treatment of aluminium alloys, its scope of applications has since then been extended to various metallic materials such as Mg, Ti, Zr, Hf, Nb, brass, and steels. The resultant coatings are in use for decorative, functional and protective applications. [3] However, especially in the case of steels, the PEO coatings provide low resistance against corrosive and tribological stresses. This is because the generated layers consist mainly of iron oxides with relatively little comprised of the more stable compounds formed
by the electrolyte constituent [4, 5, 6]. Furthermore, iron-based materials often require very high current densities between 40 [7, 8] and 300 [9, 10] A/dm$^2$, up to 3750 [11, 12] A/dm$^2$ to start and maintain the discharge process. This can be attributed to the poor passivation behaviour of the substrates used. In the context of PEO, this means that electrochemical processes dominate on the substrates under anodic polarisation in aqueous environments, which leads to substrate dissolution and oxygen development. The compounds formed from the released metal ions and electrolyte constituents, on the other hand, do not form a good electrically insulating reaction layer. This, however, would be a prerequisite for generating a strong localised potential drop between the bulk electrolyte and the substrate even at moderate current densities, which enables the formation of plasma electrolytic discharge phenomena. The few descriptions of PEO of low carbon steel under moderate current densities leading to the formation of coatings composed of mixed oxides, deal with the layer characterisation mainly [13]. However, the derivation of the electrolyte composition and investigations concerning the interplay of the substrate/electrolyte-interaction with rectifier control behaviour remain unaddressed. This impedes significantly to use them as a basis for further investigations.

Therefore, it is the aim of this study to develop an electrolyte for the PEO of low-carbon steel which allows for the formation of protective ceramic coatings composed of electrolyte constituents at moderate current densities. This could allow the transfer of excellent technological properties of oxidic protective coatings to steel substrates. According to the current state of the art, this is achieved primarily by thermal spraying of alumina or the plasma electrolytic oxidation of sprayed aluminium layers [14, 15, 16]. Direct PEO would be superior to these process routes, especially due to its good throwing power on complex component geometries. In addition, this would serve as an important intermediary step in the establishment of plasma electrolytic oxidation of steel-based material composites, which are becoming increasingly significant and applicable in lightweight construction [17, 18].

In this study, the preselection of the electrolyte composition is based on systematic polarisation measurements, which have already been proven to be suitable to evaluate the passivation behaviour of varied electrolyte/substrate combinations [3]. Afterwards, PEO experiments were carried out on low-carbon steel using optical and electrical process diagnostics. The resulting coating compositions and morphologies were characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX).

2. Experimental Procedure

The polarisation experiments were carried out in a three-electrode arrangement. A 3-mol/L Ag/AgCl electrode was used as the reference and a platinum sheet as counter electrode. The test sample prepared by CSC low-carbon steel that acted as the working electrode was located at the bottom off the cell. This setup was used in order to minimise the influence of gas bubbles, which could be released during the experiments, on the recorded data. The electrolyte volume was 250 ml, and the diameter of the active sample area was 10 mm. The chemical composition of CSC steel (provided by Fr. u. H. LÜLING GmbH & Co. KG) is listed in table 1.

| Table 1. Chemical composition of CSC steel, mass fraction in %. |
|-----------------|-----|-----|------|-----|-----|-----|
|                 | Fe  | C   | Si   | Mn  | P   | S   | Al  |
| balance         |     | 0.08| 0.08 | 0.38| max.| 0.020|max.| 0.025| 0.035|

An electrochemical working station Zennium in combination with a voltage booster CVB120 (both ZAHNER-elektrik, Germany) were used to apply a voltage cycle according the vertices listed in table 2 and to record the resulting current. The current limit was set to 300 mA, which
corresponds to a current density of approximately 38.2 A/dm². The compliance voltage was 120 V.

Table 2. Vertices of the potential cycle used, depicted in figure 1.

| \( n \) | 1 | 2 | 3 | 4 | 5 | 6 |
|-------|---|---|---|---|---|---|
| \( U_n/V \) | 0 | 100 | 100 | 0 | 100 | 0 |
| \( t_n/s \) | 0 | 100 | 220 | 320 | 420 | \( \approx 420 \) |

Figure 1 shows a graphical representation of the two main types of measurement courses observed in this study. In case of poor passivation, the substrate forms no or just an unstable electrically resistive passive film in interaction with the electrolyte. The system under investigation reacts with a high flow of charge carriers and in excess of the current limit at a characteristic voltage (figure 1 a). This value is assigned as the breakthrough voltage \( U_b \) in this work. It should not be confused with the critical voltage for discharge initiation, sometimes termed breakdown or ignition voltage. An increase of the \( U_b \) voltage can be interpreted as a slight if still insufficient improvement in passivation. In case of better passivation, the experiments can be carried out completely (figure 1 b).

The integration of the current over defined time ranges (see table 2) according equation (1) leads to a characteristic \( \sigma \)-value which can be used to quantify the observed passivation behaviour. Its lowering indicates an improved passivation.

\[
\sigma = \int_{t_2}^{t_3} i(t) \, dt
\]

The test samples where pretreated by grinding on 4000 cm² paper, pickling in 1:1 hydrochloric acid, and then rinsing with deionised water. The electrolytes were solutions of disodium hydrogen phosphate and sodium aluminate with concentrations between 0.3 and 1.5 mol/l and varied pH values. The alkalinity was lowered through the addition of phosphoric or citric acid and elevated by potassium hydroxide solution. Table 4 and 5 list the investigated electrolyte compositions. All chemicals used were analytically pure (Merck, Germany). The PEO experiments were carried out within an electrolyte container with a volume of 5 litres.
The solution was circulated by a mechanical stirrer and cooled by water of 5 °C that was circulating around the container. The cylindrical test samples had a diameter of 16.5 mm and a height of 10 mm. In order to avoid an interaction with the discharge phenomena, the specimen holder made of aluminium was covered with shrink tubing and pressed into a stepped bore in the lateral surface of the sample. Its geometry is depicted in figure 2 a. Figure 2 b shows the approximate position of the places where the SEM images depicted in figure 8 and 9 were taken.

![Technical drawing of the sample geometry (a) and approximate position (Pos. 1 and 2.) of the places where the SEM images shown in figures 8 and 9 were taken.](image)

Figure 2. Technical drawing of the sample geometry (a) and approximate position (Pos. 1 and 2.) of the places where the SEM images shown in figures 8 and 9 were taken (b).

A **POWER PULSE** pe861UA-500-10-24-S rectifier (plating electronics, Germany) was used to apply a symmetric current-controlled alternating rectangular pulse, the parameters of which are summarised in table 3. The values of $U_1$ and $U_2$ represent the anodic and cathodic voltage limitation. Figure 4 a contains a corresponding graphical representation.

**Table 3.** Parameters of the symmetric current-controlled alternating rectangular pulse for PEO.

| $I_1$/A | $i_1$/A·dm$^{-2}$ | $t_1$/ms | $U_1$/V | $I_2$/A | $i_2$/A·dm$^{-2}$ | $t_2$/ms | $U_2$/V |
|--------|-----------------|----------|---------|--------|-----------------|----------|---------|
| 1      | 25              | 5        | 500     | -0.5   | -12.5           | 5        | -500    |

The process showed a severely delayed discharge initiation of up to 25 min, even with the optimised electrolyte used. Therefore, the alternating regime was preceded by a voltage-controlled DC staircase in order to support the formation of an initial passive layer. Here, the voltage was elevated in steps of 25 V with a duration of 25 s per step up to 425 V over a time period of 7:05 min. The electrical process data were monitored by using a *DL850* transient recorder (Yokogawa, Japan). The voltage was tapped directly at the electrodes with a 10:1 probe. The current signal was determined by recording the voltage drop over a shunt resistor (Isabellenhütte, Germany) of 0.1 Ω tied into the circuit. In order to obtain integral optical process informations in temporal synchronisation with the electrical process data, a photo diode was placed close to the steel sample. The device was mounted in a BNC-adapter and contained in a glass cylinder with darkened lateral surface. The photo voltage courses generated during the PEO were monitored with the transient recorder as well. Its measurements were triggered by the rise of the voltage edge over a level of 10 V every 10 seconds and were carried out with a sampling rate of 1 MS/s over 100 ms. Afterwards, the resulting data were processed by using a low-pass filter with a cut of frequency of 15 kHz, by using a MATLAB tool. Additionally the discharge phenomena during the experiments were filmed with a *Gopro Hero 5* camera (Gopro, USA), which allows for a spatially resolved characterisation of the process.
The XRD investigations were carried out with a D8 Discover (Bruker AXS, USA). The samples were measured with Co-Kα radiation (40 kV, 40 mA) with point focus using a 0.5 mm collimator and a LynxeyeXE-T detector over an exposure time of 9.5 h. The phase allocation was based on the PDF-2 Release 2014 database of the International Centre for Diffraction Data (ICDD). The layer’s morphology was made visible for selected examples with a scanning electron microscope 1455VP (LEO, Germany) using an excitation voltage of 25 kV based on secondary electron (SE) mode. The chemical composition was determined with an energy-dispersive X-ray spectroscopy system which was part of the experimental setup.

3. Results

3.1. Polarisation Experiments

The $U_b$ values determined in the first series of polarisation experiments are listed in table 4. The pH was adjusted from its initial value by the addition of phosphoric acid or potassium hydroxide solution respectively. In the case that the electrolyte conductivity was so low that the compliance voltage of the booster was exceeded during the measurement the solution is marked with the ◦-sign. Electrolytes which precipitate during or shortly after the preparation are provided with a †-symbol. Electrolytes which allowed for the complete polarisation experiment and the determination of the $σ$-value are indicated by sigma. The statistical deviations of these measurements were less than 1 % and are not listed for the sake of clarity.

Table 4. Results of the first series of polarisation experiments.

| substance | KOH | Na$_2$HPO$_4$ | NaAlO$_2$ |
|-----------|-----|---------------|-----------|
| $c$/mol·l$^{-1}$ | varied | 0.5 | 1.0 | 1.5 | 0.5 | 1.0 | 1.5 |
| pH$_{\text{initial}}$ | 8.7 | 8.6 | 8.6 | 12.7 | 12.8 | 13.0 |
| $U_b$/V | | | | | | |
| pH$_{\text{adjusted}}$ | 9 | 7 | 15 | † |
| 11 | 6 | 6 | 5 | † |
| 12 | ◦ | 6 | 4 | 4 | σ | σ | σ |
| 13 | 11 | 4 | 3 | † | 29 | 31 | 31 |
| 14 | 2 | 2 | † | † | 2 | 0.4 | 0.3 |

◊: conductivity too low; †: precipitation; σ: completed measurement (see table 5)

It can be seen that the phosphate electrolytes led to poor passivation behaviour even when directly compared to pure potassium hydroxide solution. The $U_b$ values are between 2 V at pH = 14 and 15 V at pH = 9. In contrast to those within the aluminate electrolytes, breakthrough voltages of around 30 V can be achieved at pH = 13, while at a pH of 12 the polarisation experiment can be carried out completely. The corresponding $i(t)$ courses are depicted in figure 3 a. Inconveniently, it was unfeasible to prepare a volume of five litres for practical PEO experiments with the equivalent amount of phosphoric acid. The pH did not fall below 12.3. Further addition of phosphoric acid led to precipitation of the solution. This can be attribute to the buffering point of phosphates in this pH range.
Therefore, a second series of polarisation experiments was carried out with aluminate solutions, the pH of which was adjusted by the addition of citric acid. Since electrolytes of 1 mol/l precipitated during this procedure, the experimental range was extended to 0.3 and 0.1 molare concentrations. The resulting $i(t)$ courses are depicted in figure 3 b. Table 5 summarises the experiments of the aluminate solutions with a pH of 12 and the determined $\sigma$-values.

| substance $\text{Na}_2\text{AlO}_2$ c/mol·l$^{-1}$ | 0.1 | 0.3 | 0.5 | 1.0 | 1.5 |
|-----------------------------------------------|-----|-----|-----|-----|-----|
| $\sigma$/As·dm$^{-2}$ pH = 12 by $\text{H}_3\text{PO}_4$ | 473 ± 14 | 318 ± 46 | 484 ± 213 |
| pH = 12 by $\text{C}_6\text{H}_8\text{O}_7$ | 418 ± 52 | 495 $^*$ ± 6 | 531±8 $^*$ |

$^*$: precipitation, $^*$electrolyte for the practical PEO experiments

The data only allow a statement regarding the influence of the substance used for pH adjustment on the resulting passivation behaviour for 0.5 molar solutions. The use of citric acid led to a slight deterioration. However, the $\sigma$-value decreased from 531 As/dm$^2$ to 418 As/dm$^2$ if the concentration was lowered down to 0.1 mol/l.

For the subsequent PEO experiments the solution of 0.3 mol/l aluminate with a pH of 12 adjusted by citric acid and a $\sigma$-value of 495 As/dm$^2$ was selected. This is a compromise between
as-high-as-possible concentration for the better incorporation of electrolyte constituents into the layer, and the aim to initiate and maintain the plasma electrolytic discharges at moderate current densities by good passivation.

3.2. PEO process

Figure 4 shows typical recorded process informations at a PEO treatment time of 15 minutes after the initial voltage staircase. The data are represented with a temporal resolution in the range of milliseconds, which allows for the detailed evaluation of the generated pulse shapes.

![Graphical representation of the electrical pulse regime at 15 minutes of PEO treatment after initial voltage staircase: process-voltage (a), current-density (b), and photo-voltage (c) along with the associated limits, definitions, and pre-discharge values. These (a-c) are then summarised into a voltage current density-characteristic (d), with photo-voltage indicated by colour, combined with a image of the process.](image)

In figures 4 a and b, the measured process-voltage and current-density patterns are depicted. Furthermore, the anodic voltage limitation and the shape of the predefined current-controlled pulse are marked by additional dashed lines. It can be seen that the set-point values are not achieved either during the anodic or the cathodic partial pulse. While the predefined current density is almost reached at the end of the positive half cycle, the following pulse part leads to polarity reverse only barely. The voltage curve shows a flattening at the end of the anodic partial pulse, which can be attributed to the approaching of the voltage limitation. In contrast, the amount of voltage change in the cathodic partial period remains largely constant. Figure 4 c shows the corresponding course of the photo-voltage which is proportional to the light emission. The horizontal dashed line at $U_{\phi pd} = 0.36$ V marks the photo-voltage value measured during the pre-discharge stage at the beginning of the experiment. The $U_{\phi pd}$ value can be attributed to background brightness of the experimental setup. It can be seen that rises of the photo voltage and thus discharge phenomena take place during the anodic partial pulse only. Despite
the transition between the extremes being rather smooth, $U_{\text{opd}}$ is achieved regularly during the cathodic partial pulse. This indicates a meantime interruption of the discharge phenomena.

Figure 4 d shows the combined data of 4 a–c without the time information. Furthermore, a screenshot of the process video is included in the diagram. The electrical process data are plotted according to a voltage–current-density characteristic (VCC) with the $U(i)$ curve. The grey arrows indicate the forward feed direction. The intensity of the measured photo voltage is depicted by the line colour and addressed by the corresponding colour bar. The achieved voltage and current density extremes are marked (by the anodic and cathodic reversal points $P_{\text{ar}}$ and $P_{\text{cr}}$) as well as a characteristic voltage in the descending branch of the VCC where the current density is zero, which is referred to as the threshold voltage $U_{\text{th}} = 27$ V. It is thought that this value contains information regarding the PEO layers morphology and is rising with descending defect density [19]. Furthermore, an initial anodic peak (i. a. p.) can be observed in the rising branch of the $U(i)$ curve. Since the photo voltage is still in range of the $U_{\text{opd}}$ value, this section can be attributed as belonging to the pre-discharge stage of the pulse. Therefore, the underlying processes are electrochemical and not plasma chemical in nature. While the ascending and descending branches are largely congruent in the later part of the $U(i)$-course, another loop appears around the anodic reversal point. Since the photo voltage assumes maximum values here, i.e. intense discharge phenomena take place, the system behaviour can be attributed to plasma chemical processes. The screenshot shows mainly two bright discharges, which illustrates a strong spatial localisation of the discharge phenomena.

Figure 5 represents the course of the characteristic values defined in 4 d as dependent on the process time. Additionally, the anodic voltage limitation, the predefined current-density extremes, and the $U_{\text{opd}}$ value are depicted by dashed lines.

**Figure 5.** Course of the process voltage and current-density extremes (a) as well as the maximum and minimum values of the photo voltage (b) as dependent on the process time.
In figure 5 a, it can be seen that the anodic voltage limit is reached after about one minute, while the minimum voltage hardly reaches cathodic ranges over the entire process time. The current-density extremes show a similar behaviour in regards to reaching of the predefined vertices. The regularly occurring drops of the maximum values are noticeable, which coincide with more pronounced minima, which sometimes reach the negative range. Direct comparisons to the behaviour of the photo-voltage extremes, depicted in figure 5 b, show that these occur in temporal synchronisation with drops of the maximum photo-voltage, which can be attributed to ”darker” process phases. The value of the minimum photo-voltage is in range of $U_{\phi pd}$ during the entire process time. Hence it can be concluded that the discharges are interrupted regularly by the applied electrical regime.

The process-time dependent development of the discharge behaviour is shown for the initial DC voltage staircase in figure 6 and for the subsequent alternating pulse regime in figure 7. The photo series are based on the recorded video and allow for qualitative statements regarding the initiation and spatial distribution of the discharge phenomena. As can be seen in figure 6, plasma electrolytic discharge phenomena occurred for the first time at a DC voltage of 300 V. As the voltage was further increased up to a maximum potential/value/voltage of 425 V, the light emission from the sample likewise increased.

**Figure 6.** Process photo series of a PEO process during the initial DC voltage staircase with a 25 V step every 25 s, with each individual photo labelled with the applied voltage.

**Figure 7.** Process photo series of a PEO process during the alternating current-controlled pulse regime labeled by the process time in the mm:ss format.

During the subsequent PEO regime under alternating polarisation, the discharges initially came to a standstill, firstly. This can be seen in the first picture of the series in figure 7 and the low
photo voltage in this process stage (5 b). After approximate 10 seconds, the discharges started again. Further experiments performed without the DC voltage staircase at the beginning or with lower maximum voltage during the DC stage (not presented in this study), showed much more pronounced delay in discharge initiation. Further on in the process, the discharge pattern remains largely qualitatively the same. There are rarely more than two or three discharges on the visible sample front. These move slowly over the substrate surface and burn for 5 to 30 seconds. In addition to the discharges, the video recordings seem to show significant gas evolution along the sample surface apart from the discharges. Unfortunately, this partial aspect cannot be clearly substantiated from the images due to their insufficient quality.

3.3. Coating characteristics

Micrographs of selected coating sections obtained by the SEM investigations are depicted in figure 8 and 9. Their respective extraction points are shown schematically in figure 2 b. Based on ten measurements of the sample extracted from position one, the layer thickness can be specified with an average of about 83 µm with a standard deviation of 4 µm. The coatings show a poor substrate bonding, and their microstructure seems to consist of two different constituents, one looking "glassy" with elongated defects, and one looking "foamy" with globular defects. While the characteristic areas are next to each other in Figure 8, a layered structure can be seen in Figure 9.

The results of the XRD measurements, shown in figure 10, indicate an absolute dominance of the α-Al₂O₃ corundum phase of approximate 90%. Hence, the particular microstructure cannot be explained by the presence of different phases. In order to trace the development of the layers phase composition during the process, additional PEO experiments were carried out with treatment times of 0, 10, 20, 30, and 40 minutes after the initial DC voltage staircase. It can be seen that α-Al₂O₃ is already present at the beginning of the process. The data clearly show that the layer consists almost exclusively of crystalline aluminium oxide, mainly the α- and η-phases. However, it was not possible to definitely assign a percentage of the layer composition to the two components.

![Figure 8](image_url)

**Figure 8.** SEM images of the PEO coating at the sample’s lateral surface (pos. 1 in figure 2 b), showing a microstructure consisting in two different areas with elongated and globular defects, arranged side by side.
Figure 9. SEM images of the PEO coating at the samples top surface (pos. 2 in figure 2 b), showing a microstructure consisting in two different areas with elongated and globular defects, layered over each other.

While the visual appearance of the diffraction patterns indicate an absolute dominance of corundum, the software-supported evaluation lead to a ratio of 1:1 for the two phases. Iron oxides or other iron compounds formed with the electrolyte are not detectable. Therefore, the PEO, which in most of its variants is a conversion procedure, was successfully transferred into a deposition process. EDX measurements in both types of coating regions showed a composition of 56 % O and 43 % Al (atomic percent), which indicates Al₂O₃.

Figure 10. X-Ray diffractograms of PEO coatings obtained after different treatment times between 0 and 40 min after the initial DC voltage staircase, measured at the sample top area (position 2 in figure 2).
4. Discussion

The results of the polarisation experiments show that the systematic electrolyte variations led to an improved passivation on C8C steel. For aluminate electrolytes, it was possible to carry out complete measurements at moderate alkalinity of pH = 12. However, the $\sigma$-value of the electrolyte used for the practical PEO experiments in this study is, with 495 As/dm$^2$ still two times above the range which has been proven suitable for PEO experiments on Aluminium [20]. Therefore, the exhibited passivation behaviour may still be insufficient.

This presumption is supported by analysis of the process data shown in figure 4 d. The significant electrochemical anodic peak at the ascending branch of the $U(i)$ course stands for repassivation of bare metallic regions. However, since only very limited parts of the substrate surface are in direct interaction with the electrolyte even in the case of a porous layer with poor substrate bonding, the measured currents cannot be explained by passive film growth alone. This suggests the occurrence of parasitic reactions such as anodic metal dissolution and oxygen formation. After the initial anodic peak, the $i(U)$-curve rises again, first following a linear then exponential relationship to the applied voltage. Light emission can only be detected above 400 V. Thus, the aforementioned coating-deteriorating electrochemical processes become more pronounced within this pulse stage. The plasma-chemical occurrences around and after the anodic reversal point cannot be interpreted in more depth with the experimental setup used. The descending branch of the $U(i)$ course only crosses the zero line at a very low threshold voltage of $U_{th}=27$ V. This proves that the PEO coating consisting of crystalline alumina with a thickness of approximately 80 µm must have many defects that almost reach the substrate. Otherwise, its electrical resistance and the resulting threshold voltage would be significant higher.

This assumption is confirmed by the SEM images shown in figures 8 and 9. The layer structure shown here with its inhomogeneous phase composition and poor substrate bonding differs significantly from the alumina layers on aluminium materials produced by PEO [21]. The mentioned structural defects could have originated from strong localisation of the intense and long-lasting plasma electrolytic arc discharges during the process, visible in figures 6 and 7. The regularly appearing drops in the electrical process variables and the maximum photovoltage, as depicted in figure 5, occur in temporal synchronisation, which indicates that the PEO coating is damaged and subsequently healed several times during the process. A further hint is the uneven development of the substrate-related iron peak intensity over the process time in the diffraction diagrams in figure 10. The appearance and dominance of the arc discharges can be explained by the fact that the cathodic partial pulse was applied insufficiently on the experimental setup. As it can be seen in figures 4 and 5 the process-voltage and current density barely reach negative values at the end of the pulse. The course of the photo voltage shows that this is enough to interrupt the discharges, by reaching of $U_{opt}$. However, it can be doubted that this is sufficient to repel the anions at the substrate/electrolyte interface and to pull them back evenly distributed in the subsequent anodic partial pulse. Such a homogenised distribution of the specimen along the quasi-cathode would be a prerequisite for uniformly distributed spark discharges.

According to figure 10, the particularly stable high-temperature modification $\alpha$-$\text{Al}_2\text{O}_3$ is dominant within the layer composition. Furthermore, it appears not just in later process stages as is known from PEO of aluminium [22]. This can be interpreted as a positive result of the energy-intense arc discharges.

Based on the made observations and their interpretation, the following procedure is suggested for further investigations. The selection of the electrolyte used for PEO was a compromise between the best possible passivation and highest possible electrolyte concentration in order to incorporate electrolyte constituents into the resulting layer. Since it was possible to produce layers that consisted almost exclusively of aluminium oxide, the electrolyte concentration could be reduced further in favour of better passivation. This study does not provide final experimental evidence that the bubbles visible on the process recordings originated in any
significant extent from electrochemical anodic gas formation. Since electrolyte evaporation in the vicinity of the discharges could also be the explanation, it is recommend that pulses with anodic voltage limitations below the process time dependent ignition voltage should be coupled with the electrical regime. If the gas formation persists, it can then be attributed solely to the electrochemical processes. In order to finally clarify the coatings phase structure, measurements using electron backscatter diffraction (EBSD) are recommended. A promising approach to homogenise the layer microstructure and to improve the substrate bonding is to shift the discharge behaviour in favour of more finely distributed spark discharges. Therefore, the cathodic part of the electrical regime should be more pronounced by adjusting the current value and/or the duration of the negative partial pulse.

5. Summary and conclusion
The results of this study can be summarised as follows.

- Systematic polarisation experiments have been used successfully to preselect an environment friendly electrolyte suitable for PEO of low-carbon steel.
- The resulting coatings have the following desirable characteristics:
  i) they grow fast (approximately 80 µm after 37 minutes),
  ii) consist exclusively of crystalline aluminium oxide,
  iii) and aim a high content of corundum.
- The coatings are limited in their suitability for practical applications by the following weaknesses:
  i) their inhomogeneous microstructure
  ii) and poor substrate bonding.
- The results of the electrochemical measurements and the analysis of the PEO process data indicate that this can be explained as follows:
  i) the passivation behaviour of the electrolyte is still insufficient,
  ii) to less pronounced cathodic partial pulses in the electrical regime lead to a strong discharge localisation during the PEO.
- An experimental procedure was proposed to check these assumptions and to solve the named issues.

The PEO, which in most of its variants is a conversion procedure, was successfully transferred into a deposition process in the course of this study. This allows thick, corundum-rich aluminium-oxide layers to be produced on low-carbon steel in a short process time. Further research is required to improve their technological properties. The knowledge gained can be used for the plasma electrolytic oxidation of steel and steel-based material composites.

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