Increasing the application fields of magnesium by ultraceramic®: Corrosion and wear protection by plasma electrolytical oxidation (PEO) of Mg alloys

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ABSTRACT

Due to its low density and high strength, magnesium has increasing potential in the lightweight area, especially as a material for structural components. To address the corrosion problem, which is the main issue with using Mg alloys in the automotive industry, as well as to address wear problems, a new technique that uses an asymmetric potential pulse waveform to form nanocrystalline PEO (plasma electrolytical oxidation) coatings on Mg substrates, especially on sheet Mg plates, is developed in this study.

The results of the analysis of PEO coatings on different sheet Mg alloy plates, which are characterized by electrochemical analysis methods including electrochemical impedance spectroscopy and potentiodynamic polarization are presented in this study. Furthermore, the coatings are characterized regarding their morphology and wear resistance, while varying the coating thickness by different processing times. A further improvement of the applied waveform by an on-top modification of the pulse signal leads to higher corrosion resistance as well as to a better performance in the tribological testing.

1. Introduction

The weight saving potential by using magnesium exceeds 50% for some components, which leads to an increased usage of Mg alloys in the automotive, aerospace and mechanical engineering fields in the last few years. Therefore, substituting other materials for Mg leads to a reduction in fuel and CO₂ emission [1]. Nevertheless, it is still a niche material [2] due to its challenging anti-corrosion protection [3]. Mg cast alloys are already in use in components such as gear cases or steering wheels [4] as well as in A- and B-pillars or as inner stiffening components of doors and hatches [5]. Additionally, Mg plays an important role in multi-material automotive engineering [6], which could be extended by a better control of the corrosion of its alloys.

Since Mg has the lowest electrode potential [7], galvanic corrosion in the atmospheric environment is a profound problem in the case of Mg alloys [8]. This problem is addressed by different alloying strategies using Alun [9,10], whereas alloying with Zn for improving the mechanical properties is reported to increase the effect of corrosion in comparison to Mg metal [11].

Furthermore, Mg alloy sheets exhibit poor formability at room temperature [12], leading to many efforts to increase the formability by adding elements such as Ca, Sn or rare earth elements [13–15].

Due to the great interest in using Mg alloys in manifold applications there are different efforts to perform surface treatments and coating processes to prevent corrosion. Cold spraying is one technique [16,17] that increases the corrosion resistance of Mg alloys to the range of Al bulk materials. Furthermore, conversion coating treatments with permanganate phosphate solution [18,19], anodic oxidation [20–22] in combination with sealants or galvanic deposit coatings [23] are widely used. Most of these methods create surfaces that require a post-processing such as sealing, or surfaces that cannot respond to the wear requirements [24]. With the PEO process (plasma electrolytical oxidation), crystalline ceramic surfaces can be formed on Mg alloys, which exhibit great hardness and are suitable for both: corrosion and wear resistance without any further treatment [24].

Recently, a substantial effort toward improving the PEO process on Mg alloys can be observed in the literature. Thus, the correlations between the voltage-time behaviour during the coating process and PEO performance [25], the role of particle addition [26–32] in the electrolyte, the influence of the electrolyte concentration [33] and the electrical parameters [34] are studied in detail.

To increase the range of applications for Mg alloys in the automotive industry a highly corrosion resistant nanocrystalline PEO coating was developed in this study based on a novel kind of electrical guidance during the PEO process, which can be applied to different alloys (AM50, AZ31 and E-Form®). With this method, the thickness can

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be varied and adapted to the application field. The novel asymmetric waveforms applied in this study differ from the waveforms reported recently to produce soft sparkling PEO processes, which are characterized by an abrupt increase of the anodic branch and a slow decrease of the cathodic branch [26,35,36] or by symmetric trapezium waveforms [27,37]. The use of bipolar pulsed power to achieve PEO coatings on Al alloys was recently examined in-depth by Martin et al. [38]. These authors claim that using the rising edge of the anodic current leads to a delay in the occurrence of the micro-discharges (MDs). Furthermore, these authors determined that the charge quantity ratio conditions are crucial for the coating formation. The negative pulse and a pause between the pulses were proposed to quench the MDs and inhibit their transition in destructive discharges by Matykina et al. [27].

Since the PEO process in known to be highly energy-consuming [25,27], it is desirable to decrease the overall energy consumption by e.g. shortening the process time without a degradation of the coating performance. For that reason, the PEO process was optimized for the newly observed E-Form® alloy, resulting in a thin, but enclosed and more wear- and corrosion-resistant coating.

2. Materials and methods

2.1. Materials

As sheet materials, three different Mg alloys were used in this study: AM50, AZ31 and E-Form®. AM50 is a Mg-Al-Mn-system, which is known to have a high ductility accompanied by good strength [39]. In the automotive industry, it is already used for the inner lining of tail-gates in the VW Lupo [40,41] or the door inner. AZ31 consists of Mg-Al-Zn-Mn with a somewhat lower ductility but better mechanical properties at room temperature and it is one of the most widely used Mg sheet material for industrial applications [42]. By adding rare earth elements and/or Calcium to AZ31, the formability can be improved and a better creep resistance can be achieved [43–45]. POSCO developed the E-Form® alloy, which is an AZ31 with additional Ca resulting in a much higher formability than commercial AZ31B [46].

The chemical compositions of the used Mg sheet materials were examined using the XRF Olympus DELTA professional analyser, with the results shown in Table 1.

Thus, the additional Ca has a concentration of 4.35 wt% in the E-Form® alloy accompanied by lower contents of Al and Si. Singh et al. reported that the average grain size in the E-Form® alloy is 11.5 μm [12], whereas the average grain size for the as-received AZ31 alloy is reported to be 35 μm [47]. Furthermore, the E-Form® alloy was found to lead to a weaker basal-fibre structure, while the as-received AZ31 is strongly textured [12].

2.2. PEO process

The ELB ultraceramic® PEO process was carried out using a pulsed DC power source. Stainless steel was used as a counter electrode, which was formed to be component-specific, and an additivated low-alkaline aqueous solution with 4 g/l NaOH, 15 g/l Na2SiO3 and 15 g/l Na4P2O7 was used as the electrolyte. The PEO processes were performed using the waveforms shown in Fig. 1. For the original process a waveform was used, which is characterized as having an asymmetric bipolar pulse

Table 1

| Chemical compositions of the Mg sheet materials used in this study. | Al (wt%) | Si (wt%) | Mn (wt%) | Zn (wt%) | Ca (wt%) | Mg (wt%) |
| --- | --- | --- | --- | --- | --- | --- |
| AM50 | 4.52 | 1.97e−01 | 1.28e−01 | 1.81e−02 | 0 | Balance |
| AZ31 | 2.61 | 1.89e−01 | 1.46 | 7.46e−01 | 0 | Balance |
| E-Form® | 2.02 | 7.38e−02 | 1.23 | 1.14 | 4.35 | Balance |

with a controlled gradual slow increase in the anodic branch (82% duty cycle), holding the potential, and an abrupt decrease in the cathodic branch (18% negative cycle).

The ultraceramic® process, represented by the asymmetric pulse waveform shown in Fig. 1a, was applied on the AM50 and AZ31 sheet materials. In all cases, the RMS value of the potential was set to U_RMS = 290 V, and the pulse frequency was set to 500 Hz. The coating thickness was controlled by the processing time, where 3 min, 5 min and 9 min lead to coating thicknesses of approximately 10 μm (S), 25 μm (M) and 50 μm (L), respectively. Since the thinner coatings (M and S) already showed good corrosion resistance as detailed in the Results section, these thicknesses were adapted to the E-Form® sheet material. With further improvement to the coating process by using the waveform shown in Fig. 1b the optimized S-PEO coating on the E-Form® sheet was obtained. In this case, the additional on-top signal led to a more enclosed and wear-resistant coating.

Table 2

| Coating designation and conditions to produce the sample. | Coating designation | Process time/min | Process procedure |
| --- | --- | --- | --- |
| S | 3 | Asymmetric pulse |
| L | 5 |
| M | 9 |
| S opt. | 3 | Asymmetric pulse + on-top signal |

Fig. 1. Applied waveforms used for the PEO process: a) original ultraceramic® bipolar-pulsed process and, b) optimized ultraceramic® bipolar-pulsed process with additional on-top signal.
to an improvement in the coating performance. Table 2 summarizes the conditions used to perform the PEO coating.

2.3. Methods

The coated surfaces were characterized regarding their roughness and porosity using a laser scanning microscope (LSM, type: Keyence VK-X100 series) and the software VK analyse module. The obtained $R_a$ and $R_p$ values are given for every observed surface. Here, the $R_a$ (arithmetic mean deviation) value as well as the $R_p$ (maximum peak height) are recorded using a cut off wavelength of $\lambda_c = 0.80 \text{mm}$. Furthermore, the number of pores, the area ratio of the pores, their diameter and the degree of their sphericity were analysed. The obtained coating thicknesses were proven using cross-sections.

All electrochemical measurements presented were performed in a 0.1 M NaCl solution, using a three-electrode configuration, with an Ag/Ag-Cl reference electrode and a platinum-coated titanium counter electrode. The sample to be examined was operated as the working electrode. To perform the measurements, the impedance equipment of Ingenieurbuero Peter Schrems (PGU10V-1A-IMP-SR) was used and run by the software EcmWin.

For the first characterization of the samples the open circuit potential (OCP) was monitored. Electrochemical impedance spectroscopy (EIS) measurements were carried out after observing a stable state of the OCP for 10 min by varying the voltage with an amplitude of 10 mV around the OCP in the range from $10^{-2}$ to $10^2$ Hz. Equivalent electrical circuit fittings were performed using the ZView software by Scribner Associates Inc. and only fitting results with a goodness of fit of

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**Table 2**

| Sample | Coating thickness/μm | Number of pores/1e⁻⁴ cm² | Area ratio pore/% | Pore diameter/μm | Degree of pore sphericity |
|--------|----------------------|---------------------------|------------------|-----------------|--------------------------|
| S AM50 | 8.6 ± 1.7            | 128                       | 10.2             | 15.9 ± 6.4      | 0.22 ± 0.10              |
| M AM50 | 27.5 ± 4.0           | 103                       | 14.7             | 20.4 ± 7.9      | 0.20 ± 0.10              |
| L AM50 | 45.2 ± 6.0           | 77                        | 23.5             | 27.6 ± 11.3     | 0.18 ± 0.10              |
| M AZ31 | 12.2 ± 1.4           | 111                       | 8.49             | 15.6 ± 6.3      | 0.25 ± 0.09              |
| S AZ31 | 22.3 ± 4.4           | 109                       | 14.4             | 19.6 ± 7.7      | 0.20 ± 0.10              |
| L AZ31 | 41.8 ± 4.7           | 82                        | 20.0             | 25.6 ± 10.4     | 0.18 ± 0.10              |
| S E-Form | 13.4 ± 2.2         | 117                       | 12.3             | 17.4 ± 6.8      | 0.23 ± 0.11              |
| M E-Form | 24.2 ± 2.6          | 127                       | 16.7             | 19.6 ± 7.6      | 0.21 ± 0.10              |
| S opt. E-Form | 12.6 ± 2.5 | 152                       | 12.4             | 16.3 ± 6.5      | 0.23 ± 0.09              |

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![Surface structures of the PEO coatings detected by LSM: a–c) L-, M- and S-PEO on AM50; d–f) L-, M- and S-PEO on AZ31; g–h) M- and S-PEO on E-Form; i) optimized S-PEO on E-Form.](image-url)
χ^2 < 1 \times 10^{-3} were chosen to be appropriate. The potentiodynamic polarization measurement of each sample was performed by increasing the potential from −1800 mV to −600 mV (against Ag/Ag-Cl) with a velocity of 1 mV/s. Every measurement was performed three times to ensure reliability.

Some selected samples and their cross-sections were examined by scanning electron microscopy (SEM) with the Zeiss Auriga FEG at the University of Applied Sciences, Osnabrück. All presented SE micrographs are recorded at an excitation energy of 15 keV using the SESI detector for the topographical surface observations and the back-scattering mode at an excitation energy of 25 keV for examining the cross-sections and performing the EDX line scans.

As the corrosion protection of the PEO coatings and the wear performance are of high interest, the coatings were examined regarding their wear behaviour using a pin-on-disc tribometer from Anton Paar (TRBMZKO). As a counter body, a 100Cr6 ball with a diameter of 6 mm was used. The tribometer was operated in the oscillating mode (one sliding distance of 2.5 mm) with a top load of 4 N. The measurements were performed in dry conditions at ambient pressure and stable humidity conditions. The resulting wear traces were observed using the LSM for analysing the topography and depth profile.

3. Results

3.1. Microstructure and composition

Fig. 2 shows the microstructures of the PEO surfaces recorded using the LSM. All micrographs were recorded using the same amplification. Obviously, for all three alloys, the topographical microstructure of the surface becomes finer as coating thickness decreases. This result is in agreement with the process of PEO, in which applying the current density for a longer time leads to more discharge events on the substrate surface and, thus, to a higher roughness [48]. The optimized S-coating on the Mg E-Form® sheet, performed using the on-top modified waveform shown in Fig. 2i, exhibits a very fine structure.

From Table 3, one can conclude that by increasing the coating thickness the overall amount of pores (and cracks, which are also identified as pores, if they are large enough) decreases accompanied by an increase in the pore area ratio. Thus, the pore diameter also increases. Furthermore, the sphericity decreases for thicker coatings compared to thinner coatings. The original process on the E-Form® alloy shows almost the same results as on the AZ31 alloy, except that the pore area ratio is somewhat higher. Using the optimized process on E-Form®, smaller pores can be detected on the PEO surface. For all three alloys the achieved coating thicknesses are comparable for the different processing times.

All roughness values are the average values from three measured areas and are presented in Fig. 3. Hence, the Rp value represents the height of peaks above the core roughness of the coating and may be a measure for the wear of the contacting body in a tribological system [49] or of the height of the coating that may be embedded during a running-in operation [50]. Additionally, a high Rp value may be linked with a high coefficient of friction. The deviation of the Ra values is demonstrated as a shadow in Fig. 3. As seen in Fig. 3, for all three alloys, AM50, AZ31 and E-Form®, the Ra and Rp values increase with increasing coating thickness. The deviation of the values increases with the increased coating thickness as well, which is in agreement with porosity results, in which smaller and homogeneously distributed pores lead to homogeneous roughness values. These observations are in agreement with several publications [48,51,52]. Hussein et al. [51] suggest that the MD events, which eject molten oxide from the coating/substrate interface into the coating surface, become more powerful and less frequent by applying a thicker coating. Strong discharges lead to larger channels accompanied by a longer duration of the molten zone [53]. In the case of the thinner coatings (S and M), the positive influence of the rising anodic current in the PEO process, reported in [38] gains importance in terms of a smoother surface. Furthermore, the positive influence of the coating performance by applying a cathodic current in the case of the PEO process on Al [54] could be reproduced here on the Mg alloys.

It can be observed that the same PEO procedure leads to smoother coatings on the E-Form alloy in terms of both the Ra and Rp values, while the PEO coatings on the AZ31 alloy show the highest roughness values.

The optimized coating on the E-Form® alloy shows the lowest values for Ra and Rp and the visual impression of the micrographs in Fig. 2i can be emphasized. The optimization of the coating process leads to a smoother surface, which exhibits a superfine microstructure.
Fig. 5. SEM of cross-sections with EDS line scans.
Table 4
Fitted electrical parameters of EIS spectra.

| Sample  | CPE\textsubscript{out,T} (S s\textsuperscript{-1} cm\textsuperscript{-2}) | CPE\textsubscript{out,n} | R\textsubscript{out} (Ω cm\textsuperscript{2}) | CPE\textsubscript{in,T} (S s\textsuperscript{-1} cm\textsuperscript{-2}) | CPE\textsubscript{in,n} | R\textsubscript{in} (Ω cm\textsuperscript{2}) |
|---------|-----------------------------|-----------------|------------------|-----------------------------|-----------------|------------------|
| S AM50  | 6.51 × 10\textsuperscript{-7} | 0.72            | 4.24 × 10\textsuperscript{4} | 1.16 × 10\textsuperscript{-4} | 0.84            | 3.34 × 10\textsuperscript{4} |
| M AM50  | 1.76 × 10\textsuperscript{-8} | 0.90            | 2.62 × 10\textsuperscript{5} | 5.99 × 10\textsuperscript{-8} | 0.68            | 2.26 × 10\textsuperscript{5} |
| L AM50  | 6.39 × 10\textsuperscript{-8} | 0.77            | 8.84 × 10\textsuperscript{5} | 2.73 × 10\textsuperscript{-8} | 0.75            | 1.00 × 10\textsuperscript{5} |
| S AZ31  | 1.76 × 10\textsuperscript{-8} | 0.99            | 2.13 × 10\textsuperscript{5} | 1.12 × 10\textsuperscript{-7} | 0.77            | 2.11 × 10\textsuperscript{5} |
| M AZ31  | 1.22 × 10\textsuperscript{-8} | 0.99            | 1.35 × 10\textsuperscript{5} | 1.50 × 10\textsuperscript{-7} | 0.72            | 3.23 × 10\textsuperscript{5} |
| L AZ31  | 9.48 × 10\textsuperscript{-8} | 0.80            | 2.58 × 10\textsuperscript{5} | 7.63 × 10\textsuperscript{-8} | 0.74            | 2.26 × 10\textsuperscript{5} |
| S E-Form| 1.20 × 10\textsuperscript{-8} | 0.99            | 2.14 × 10\textsuperscript{5} | 8.56 × 10\textsuperscript{-8} | 0.74            | 1.53 × 10\textsuperscript{5} |
| M E-Form| 2.82 × 10\textsuperscript{-7} | 0.74            | 4.25 × 10\textsuperscript{5} | 2.59 × 10\textsuperscript{-7} | 0.99            | 3.97 × 10\textsuperscript{5} |
| S opt. E-Form | 7.21 × 10\textsuperscript{-9} | 0.99          | 3.77 × 10\textsuperscript{5} | 5.30 × 10\textsuperscript{-8} | 0.73            | 2.34 × 10\textsuperscript{5} |

Fig. 6. EIS measurements as Bode plots for the AM50 (a), AZ31 (b) and E-Form® (c) alloy with the three different PEO coating thicknesses. c) Also contains the optimized PEO coating.

A. Buling and J. Zerrer
Surface & Coatings Technology 369 (2019) 142–155
147
SEM micrographs of the pore structure of the PEO surfaces draw the same picture: The optimization of the PEO process on the E-Form® surface leads to a decrease of the pore size by compared to the same thickness coating in the original process (Fig. 4).

Fig. 5 shows the BSE micrographs of the cross-sections of the PEO coatings accompanied by EDX line scans to analyse the chemical composition. All coatings on AM50 and AZ31 alloys show a sharp increase of the O concentration at the interface between the substrate and the coating indicating a barrier layer. Additionally, an increase of the Al concentration toward the coating from inner to outer part can be observed for all performed PEO coatings, which indicates the presence of Aluminium oxide phases at the coatings’ surface. The alloying elements like Mn and Zn also show an enrichment at the coating’s surface. This is also the case for Ca in the case of the PEO coatings on the E-Form® alloy.

The morphology differs for the different coating thicknesses and the different alloys: The L-coating on the AM50 alloy exhibits a high amount of very fine channels, which are interconnected, but do not reach the substrate surface. A comparable picture is drawn by the L-coating on the AZ31 alloy. Just the coating’s top layer differs in the concentration of Mg and P, which are higher in the case of the L-coating on AM50. In the case of the M-coating on AM50 there can be found wider internal pores, but a lower number of channels compared to L-coating. The M-coating on AZ31 leads to a thicker porous outer layer, while the inner layer is almost channel-free. The morphology of the M-coating on the E-Form® alloy is comparable to that on AZ31, just the inner layer is somewhat thicker. In the case of the S-coating the AM50 alloy exhibits an open-pored outer layer and only a thin inner layer. In the case of the AZ31 alloy the outer pores are smaller and the dense inner layer is thicker. In the case of the E-Form® alloy the S-coating shows deep pores and channels almost down to the substrate. The optimized S-coating on the same alloy leads to a coating, which shows no large pores in the outer layer. The dense inner layer is thick and exhibits only slim channels without any pores. The optimized process leads to a coating with decreased discharging channels in the outer layer, while the surface remains smooth in this case.

According to the literature, the morphology of the PEO coatings consists of a mixture of pancake-like structures surrounded by a sponge-like structure [38,55]. The pancake structure is associated with discharging channels with a diameter of 5–30 μm in the centre of the pancake, while the sponge-like structure is characterized by pores with a diameter of 0.1–1 μm [38]. In the results presented here, it is obvious that the original process on the E-Form® alloy leads to a more pancake like structure, while the optimized process shows a morphology with an upward trend to the sponge-like structure.

3.2. Electrochemical measurements

EIS measurements were carried out after achieving a stable state of the OCP for 10 min in a 0.1 M NaCl solution and are represented here in the Bode plots. The equivalent electrical circuit, shown in Fig. 7, was successfully used to fit the EIS results of all of the PEO-coated samples. In this circuit, $R_s$ represents the solution resistance, while $R_{out}$ and $R_{in}$ represent resistance of the porous outer and dense inner layers,
respectively. The CPEs are the corresponding constant phase elements, which are described by

\[ Z_{\text{CPE}} = \frac{1}{Y_0(\omega)^n} \]

where \( \omega \) is the angular frequency and \( Y_0 \) the admittance constant. The exponent \( n \) can vary from 0 to 1 and is related to the roughness and heterogeneity of the surface. Such models are also used in the recent literature for PEO coatings on Mg substrates [56,57]. The fitting results are represented in Table 4.

The results for the AM50 alloy in Fig. 6a indicate that the PEO coating with an \( \sim 25\mu m \) (M) coating thickness leads to the highest impedance value at the low frequency limit (\( |Z(0.01\ Hz)| = 1.89 \times 10^7 \ \Omega \ \text{cm}^2 \)). In the case of the phase a high phase value at the high frequency limit, a broad shape of the curve and a high phase value at the mid phase range indicate a good corrosion resistance. All of these points are also fulfilled in the case of the M-coating on AM50 and can be correlated with the morphology of this coating (Fig. 5), which shows internal pores and a decreased number of discharging channels. The thinner coating (~10\mu m, S) clearly shows lower values for \( |Z(0.01\ Hz)| \) and the phase shifting at high and middle frequencies, which is in agreement with the deep porous outer layer and the thin dense inner layer seen in Fig. 5. Surprisingly, the thickest coating (~50\mu m, L) shows somewhat lower values than the M-coating. Taking into account the microstructure and the morphology (shown in Figs. 2 and 5) the picture can be made clearer: The rougher structure of the thicker coating does not lead to a better but to decreased corrosion resistance due to larger plasma discharging effects during the longer coating process (see Table 3). The inner dense layer of the L-coating shows a net of discharging channels, which can be penetrated by the electrolyte. This result is also in agreement with the fitting results, where the resistance for the dense inner layer (\( R_{in} \)), which is responsible for the corrosion protection, shows the highest value for the M-coating on AM50. Here, the \( R_{in} \) and \( R_{out} \) values are higher than those reported for unsealed PEO coatings on AM50 alloy produced by using a pulsed DC power source [29].

Similar EIS results were obtained by M. Grabowski in his PhD thesis, in which he compared different systems on AM50 and AZ91 alloys [58] and the ultraceramic coating systems performed best. With the presented M-PEO coating on the AM50 alloy, the EIS values are in a range of a PEO combined with a thick polymer coating on AZ31, as was reported by Sririvasan et al. [59].

In Fig. 6b, the EIS results for the neat and coated AZ31 alloy are shown. For the three PEO coated samples the behaviour of the curves is very similar, leading to the conclusion that all three coatings result in comparable corrosion protection in terms of self-corrosion. The S-coating shows a somewhat thinner shape in the phase (Fig. 6b). Nonetheless, high corrosion protection is expected for this sample. The impedance values for all three coating systems are slightly higher compared to those reported by Sririvasan et al. where the coating thickness seems to be comparable with our M and S systems [59]. The L-coating on AZ31 also shows slightly lower values than the M-coating, which is in accordance with the results of the PEO coatings on the AM50 alloy discussed previously; this finding is also in agreement with the study of Zhao et al. [60], who found that the corrosion resistance increases with the coating process time until an optimal value and then decreases if the process time exceeds this optimum value, which can also be linked with the coating morphology. The longer processing time leads to more MD events, which are due to the dielectrical breakdown during the coating process. These types of discharging events, called B-type discharging by Hussein et al. [51], that originate at the metal-oxide interface, show the pancake structure with a crater-like structure with central holes, which is common for the L-coatings on AM50 and AZ31 alloys. Such structures lead to a decrease in the corrosion protection because the electrolyte can penetrate the coating more easily and, thus, cause corrosion at the metal-oxide interface. This assumption could be supported by the CPE fitting results, which show the lowest values for the outer layer in the case of the M-coating on the AM50 and AZ31 alloys.

Considering that the E-Form® alloy is seen as an optimized AZ31 alloy (by additional Ca), only the thinner PEO coatings (M and S) were applied to that alloy, since those thicknesses seem to perform well.
enough in the anticorrosion behaviour and a thicker coating does not lead to a better performance.

The EIS results are shown in Fig. 6c. The results for the M-coating are comparable to those of PEO on AZ31, while the S-coating leads to somewhat lower values of $|Z|_{(0.01 \text{ Hz})}$ in the case of the E-Form® alloy. This result can be explained by the morphology of the S-coating on the E-Form® alloy (Fig. 5), where deep pores and channels can be found also in the inner layer of the coating. The optimized process (on-top bipolar pulsed waveform) leads to a S-PEO coating on the E-Form® alloy with higher values for $|Z|_{(0.01 \text{ Hz})}$ as well as for the phase value in the high and middle frequency range. The cross-section analysis of that coating explains this result: Almost no pores can be found in the outer layer of that coating. Furthermore, the inner layer shows just slim channels. Therefore, one can conclude that the optimization leads to a coating performance that is high in terms of corrosion resistance.

The fitting results of the optimized S-coating on E-Form® show increased resistivity values for both, the inner and outer layer, with a clearly decreased CPE value for the outer layer.

Drawing a connection with the morphological characteristics of the coatings the sponge-like structure, which is dominant in the optimized PEO process on the E-Form, leads to a better prevention of the penetration of the electrolyte to the metal surface. The MDs, which dominate this coating process are nominated as type A and type C micro-discharges by Hussein et al. [51]: Both of these MDs are proposed to be due to gas discharging events at the oxide-electrolyte interface, where type A describes discharges in small holes near the surface and type C discharges more deeper in the micropores. The cross-section figure of the optimized E-Form PEO shows more C-like channels, which prevent the electrolyte from penetrating the inner dense layer.

The results of the potentiodynamic measurements of the uncoated
and PEO-coated samples are shown in Fig. 8, in which the current density versus the voltage is presented. Fig. 8d contains the results of the corrosion current densities (icorr) and corrosion potentials (Ecorr) obtained from the Tafel plots of the PEO coated samples.

The corrosion behaviour of the neat AM50 and AZ31 alloys has already been studied in the literature [7,61]. Electrochemical characterization showed that the die-cast Al-Mg alloys, such as AM50, show less corrosion surface propagation than the AZ31 alloy [62]. From the obtained results, the neat AM50 alloy shows a lower corrosion current density in the anodic branch and a longer passive area until the breakthrough potential than the AZ31 alloy, which supports the results found in the literature. The neat E-Form® alloy shows a further increase in the corrosion current density and a quenched passive area. Thus, the E-Form® alloy is expected to have the poorest corrosion resistance among the observed Mg alloys. Therefore, a prevention of corrosion by PEO coating is crucial.

The corrosion potential (Ecorr) decreases from L to M and has the most noble value for the thinnest S-coating in the case of the AM50 alloy. Furthermore, the corrosion current density (icorr) (shown in Fig. 8d) for the M-coating on AM50 is lower than those of the S and M thicknesses by an order of magnitude. This result indicates a much lower hydrogen evolution through water reduction (cathodic current density) [63]. Therefore, these potentiodynamic results underline the corrosion current density decreases by an order of magnitude, accompanied by a shift of the corrosion potential to a more noble value for the S thickness and leading to a prediction of higher corrosion protection in the case of contact corrosion. Thus, this optimized S-coating on E-Form® is thick and dense enough to prevent the metal surface from corroding by acting like a physical shield [60]. Comparing the original and optimized PEO coating performance on the E-Form alloy the current density in the anodic region is one order of magnitude lower for the optimized case making this coating more resistant against localized corrosion. Therefore, the effect reported by Hakimizad et al. [35] to create a more compact inner layer with high corrosion resistance using a bipolar regime on Al substrates could be increased by using the optimized process with the on-top waveform guidance on the E-Form® alloy.

3.3. Wear behaviour

Pin-on-disc tests were performed on the different samples with coating thicknesses of ~10 (S) and 25 μm (M). The coefficient of friction (COF) was monitored for a sliding distance of 80 m for all samples. Since the thin coatings (S and M coatings) show a high corrosion protection, only these samples were chosen for the wear tests due to efficiency considerations: production of thin coatings leads to a lower energy consumption, and thus, thinner coatings, which perform well, are promising candidates.

Fig. 9a–c show the development of the COF for all the tested samples. All samples start with a low COF, which increases after approximately 2 m of sliding distance to a high but stable state. Such a behaviour was also reported for PEO coatings on Mg alloys by Rapheal et al. [64] and explained by the continual renovation of the contact area and, thus, an accelerating chemical interaction in that area. All of the tested coatings show this stable state value of the COF until the end of the testing, and thus, all of the coatings show no failure within the applied testing conditions. It is obvious that in the case of the PEO coatings on AM50 and AZ31, there is no significant difference in the COF for the two tested thicknesses, which is in agreement with the Rmax values for these four coating systems shown in Fig. 3. However, a correlation between the increasing Rmax value and the COF for the M coatings cannot be found. In the case of the E-Form® alloy the M-coating shows a somewhat different behaviour: a decrease in the COF is measurable at approximately 30 m of sliding distance. After that, not only an increase but also a rising of the signal noise is visible. This result leads to the assumption that there is a running-in behaviour followed by an uneven sliding. The main difference in the coatings’ surface composition is the concentration of Mg: While in the case of the M- and S-coatings on AM50 and AZ31 the Mg concentration decreases toward the coating accompanied by an increase in Al and O concentration, the M-coating exhibition E-Form® an increase of the Mg concentration can be observed near the coating surface. The presence of a softer MgO-phase in the coating surface may lead to the running-in behaviour and to a decreased COF.

Fig. 9d shows the average values of the COF for the tested systems, wherein the average is calculated in the quasi static area from 30 to 80 m. The shadows depict the standard deviation of the measured values. It becomes obvious that the COF values for every AM50 and AZ31 coating and the M-PEO on the E-Form® are in the same range. Surprisingly, the S-PEO on the E-Form® alloy leads to a much higher COF, which is not in correlation with the roughness measurements. The higher COFs for the S-PEO coatings on the E-Form® alloy may be linked to Ca which is added in this alloy and is enriched in the coatings surface as seen in the EDS results. Looking at the porosity values in Table 3, a correlation exists: the higher COF is, the higher are the ratio and diameter of the pores in the case of the S-PEO on E-Form®. The optimized 10 μm PEO on the E-Form® leads to a reduction in the COF, but it still remains clearly higher than those of AM50 and AZ31. All of the measured COF values are higher than those reported by Ovundur et al. for PEO coatings on 5754 Al-alloy [65] but comparable to the results of PEO coatings on mould cast Mg alloy reported by Rapheal et al. [64].

To shed light on the wear behaviour, LSM analysis of the tribologically tested samples was estimated. Therefore, an overlaid image of the optical and laser-based images was recorded accompanied by the 3D-topography. The profile lines were measured orthogonal to the corrosion.
sliding direction. The wear results of the AM50 alloy are shown in Fig. 10. For the M-coating, only a slight smoothening of the peaks is observable. The counter body (100Cr6 steel ball) experiences an abrasion in the running-in area. Fig. 11 shows the micrograph of the steel ball for the S-coating on AM50, which is exemplary for all of the other testing because the ball’s topography is comparable after any of the POD testing presented here. In all cases, the steel ball experiences an abrasive wear, which might be accompanied by the formation of an oxide tribo-layer, which leads to the highly stable state of COF in the dry sliding case [52,64].

The thin coating of ~10 μm (S) on AM50 shows an unexpected wear behaviour, namely, wear traces appear at an angle of 45° to the sliding distance. This result might be linked to the substrate topography, which plays an important role in the case of the thin coating, since the thin coating reproduces the substrate’s topography that have grinding traces in such an angle. Nevertheless, the coating is still intact and shows no wear through down to the substrate.

The wear results for the PEO coatings on alloy AZ31 are similar to those of AM50. The thicker M-coating shows only a grinding of the steel ball, where the debris is incorporated into the PEO coating. In the case of the thinner S-coating, some slight scratch marks are visible, while the steel debris gives a structure parallel to the sliding direction. These results are in agreement with the literature, where thicker PEO coatings are reported to be more wear-resistant [66] (Figs. 12).
The most impressive wear results are obtained by the PEO coatings on the E-Form® alloy. There is only smoothing of the peaks in the S-coating (Fig. 13). No wear marks can be detected on either of the coatings. In the case of the M-coating there are no topographical changes in the coating surface, which is in agreement with the low COF in that case (see Fig. 9), and only the steel ball experiences wear at the beginning of the testing phase.

The micrograph of the optimized S-coating on E-Form® shows evident a wear trace (see Fig. 14), but the 3D topography and the 2D profile show neither depth nor additional structure, leading to the assumption that the optically visible trace derives from different material reflection in this area because of to the debris of the steel ball in this area.

4. Conclusions

The work presented here investigated the corrosion and wear behaviours of PEO ultraceramic® coatings on AM50, AZ31 and E-Form® alloys formed by an asymmetric bipolar pulsed waveform. The influence of the on-top modulation of the applied waveform was studied on the E-Form® alloy.

The results can be concluded as follows:

- Ultraceramic® coatings produced by the original process show the best corrosion and wear protection behaviour for a coating thickness of approximately 25 μm (M) on all three alloys. Increasing the coating thickness by an increased process time leads to larger
discharging pores and, thus, to a lowered corrosion protection.

- The optimized ultracera® process (optimized by an on-top modulation of the process signal) leads to a smoother S-PEO coating (~10 μm) on the E-Form alloy with decreased pore diameter at the surface and sub-microstructured discharging channels. These characteristics lead to high corrosion and wear resistance despite a low coating thickness. Therefore, the energy consumption during the coating process could be reduced.

The optimization of the coating process presents a possibility to protect the novel, corrosion sensitive E-Form® alloy from corrosion and wear attacks and may increase the application field of Mg alloys.

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References

[1] E. Aghion, B. Bronfin, D. Eliezer, The role of the magnesium industry in protecting the environment, J. Mater. Process. Technol. (2001) 381–385.

[2] A.A. Luo, Magnesium development as a lightweight material—in competition with other structural materials, in: K.N. Solanki, D. Orlov, A. Singh, N.R. Neelameggham (Eds.), Magnesium Technology 2017, Springer International Publishing, Cham, 2017, p. 7.

[3] W.J. Joost, Reducing vehicle weight and improving U.S. energy efficiency using magnesium and its alloys in simulated atmospheric environments, Corros. Sci. 49 (2007) 1245–1265, https://doi.org/10.1016/j.corsci.2006.07.005.

[4] G. Song, S. Haugyna, D. St John, Degradation of the surface appearance of magnesium and its alloys in simulated atmospheric environments, Corros. Sci. 49 (2007) 1245–1265, https://doi.org/10.1016/j.corsci.2006.07.005.

[5] P. Blanchard, G. Brette, S. Subramanian, J. deVries, The application of magnesium die casting to vehicle closures, Lightweight Magnesium Technology (2005), https://doi.org/10.4271/2005-01-0338.

[6] W.J. Joost, Targeting high impact R&D for automotive magnesium alloys, in: K.N. Solanki, D. Orlov, A. Singh, N.R. Neelameggham (Eds.), Magnesium Technology 2017, Springer International Publishing, Cham, 2017, pp. 5–6.

[7] I.B. Singh, M. Singh, S. Das, A comparative corrosion behavior of Mg, AZ31 and AZ91 alloys in 3.5% NaCl solution, Journal of Magnesium and Alloys 3 (2015) 142–148, https://doi.org/10.1016/j.jma.2015.02.004.

[8] G. Song, S. Haugyna, D. St John, Degradation of the surface appearance of magnesium and its alloys in simulated atmospheric environments, Corros. Sci. 49 (2007) 1245–1265, https://doi.org/10.1016/j.corsci.2006.07.005.

[9] O. Lunder, J.E. Lein, T.Kr. Aune, K. Nisancioglu, The role of Mg17Al12 phase in the corrosion of Mg alloy AZ91, Corrosion (1989) 741–746.

[10] T.J. Warner, N.A. Thorne, G. Nuthum, W.M. Stobb, A cross-sectional TEM study of corrosion initiation in rapidly solidified Mg-based ribbons, Surf. Interface Anal. (1992) 386–392.

[11] F.-H. Cao, V.-H. Len, Z. Zhang, J.-Q. Zhang, Corrosion behavior of magnesium and its alloy in NaCl solution, Russ. J. Electrochem. 43 (2007) 837–843.

[12] J. Singh, M.-S. Kim, S.-E. Lee, E.-Y. Kim, J.-H. Kang, J.-H. Park, J.-J. Kim, S.-H. Choi, Heterogeneity in deformation and twinning behaviors through the thickness direction in E-form Mg alloy sheets during an Erichsen test, Mater. Sci. Eng. A 729 (2018) 370–384, https://doi.org/10.1016/j.msea.2018.05.072.

[13] S.-J. Kim, Y.-S. Lee, D. Kim, Analysis of formability of Ca-added magnesium alloy sheets at low temperatures, Mater. Charact. 113 (2016) 152–159, https://doi.org/10.1016/j.matchar.2016.01.013.

[14] H. Ding, X. Shi, Y. Wang, G. Cheng, S. Kamado, Texture weakening and ductility variation of Mg-2Zn alloy with CA or RE addition, Mater. Sci. Eng. A 645 (2015) 196–204, https://doi.org/10.1016/j.msea.2015.05.025.

[15] B.-C. Suh, J.H. Kim, J.H. Bae, J.H. Hwang, M.-S. Shim, N.J. Kim, Effect of Sn addition on the microstructure and deformation behavior of Mg-3Al alloy, Acta Mater. 124 (2017) 268–279, https://doi.org/10.1016/j.actamat.2016.11.020.

[16] K. Spencer, D. Fabijanic, M.X. Zhang, Cold spray of Al-MMC coatings on magnesium alloys for improved corrosion and wear resistance, MSF 618–619 (2009) 377–380, https://doi.org/10.4028/www.scientific.net/MSF.618.377.

[17] X. Xiao, X. Guo, W. Li, M.-P. Planche, R. Bolot, H. Liao, C. Coddet, Preparation and characterization of magnesium coating deposited by cold spraying, J. Mater. Process. Technol. 212 (2012) 100–105, https://doi.org/10.1016/j.jmatprotec.2011.08.010.

[18] H. Aredalean, I. Frateur, S. Zanna, A. Attrens, P. Marcus, Corrosion protection of AZ91 magnesium alloy by anodizing in niobium and zirconium-containing electrolytes, Corros. Sci. 51 (2009) 3030–3038, https://doi.org/10.1016/j.corsci.2009.03.030.

[19] Z. Shi, G. Song, A. Attrens, Corrosion resistance of anodised single-phase Mg alloys, Surf. Coat. Technol. (2006) 492–503.

[20] A. Zimmer, D. Veya-Renaux, L. Broch, N. Steim, E. Rocca, Oxide growth mechanism on mg AZ91 alloy by anodizing: combination of electrochemical and ellipsometric in-situ measurements, J. Electrochem. Soc. 164 (2017) C1059–C1066.

[21] Z. Liu, W. Gao, The effect of substrate on the electroless nickel plating of Mg and Mg alloys, Surf. Coat. Technol. 359 (2019) 414–425, https://doi.org/10.1016/j.surfcoat.2018.12.091.

[22] A. Zimmer, D. Veys-Renaux, L. Broch, N. Steim, E. Rocca, Oxide growth mechanism on Mg-3Al alloy, Acta Mater. 196–204, https://doi.org/10.1016/j.msea.2015.08.025.

[23] B.-C. Suh, J.H. Kim, J.H. Bae, J.H. Hwang, M.-S. Shim, N.J. Kim, Effect of Sn addition on the microstructure and deformation behavior of Mg-3Al alloy, Acta Mater. 124 (2017) 268–279, https://doi.org/10.1016/j.actamat.2016.11.020.

[24] K. Spencer, D. Fabijanic, M.X. Zhang, Cold spray of Al-MMC coatings on magnesium alloys for improved corrosion and wear resistance, MSF 618–619 (2009) 377–380, https://doi.org/10.4028/www.scientific.net/MSF.618.377.

[25] X. Xiao, X. Guo, W. Li, M.-P. Planche, R. Bolot, H. Liao, C. Coddet, Preparation and characterization of magnesium coating deposited by cold spraying, J. Mater. Process. Technol. 212 (2012) 100–105, https://doi.org/10.1016/j.jmatprotec.2011.08.010.

[26] H. Aredalean, I. Frateur, S. Zanna, A. Attrens, P. Marcus, Corrosion protection of AZ91 magnesium alloy by anodizing in niobium and zirconium-containing electrolytes, Corros. Sci. 51 (2009) 3030–3038, https://doi.org/10.1016/j.corsci.2009.03.030.

[27] Z. Shi, G. Song, A. Attrens, Corrosion resistance of anodised single-phase Mg alloys, Surf. Coat. Technol. (2006) 492–503.

[28] A. Zimmer, D. Veya-Renaux, L. Broch, N. Steim, E. Rocca, Oxide growth mechanism on mg AZ91 alloy by anodizing: combination of electrochemical and ellipsometric in-situ measurements, J. Electrochem. Soc. 164 (2017) C1059–C1066.

[29] Z. Liu, W. Gao, The effect of substrate on the electroless nickel plating of Mg and Mg alloys, Surf. Coat. Technol. 359 (2019) 414–425, https://doi.org/10.1016/j.surfcoat.2018.12.091.

[30] A. Zimmer, D. Veys-Renaux, L. Broch, N. Steim, E. Rocca, Oxide growth mechanism on Mg-3Al alloy, Acta Mater. 196–204, https://doi.org/10.1016/j.msea.2015.08.025.
