Final Draft
of the original manuscript:

Muhaffel, F.; Mert, F.; Cimenoglu, H.; Hoeche, D.; Zheludkevich, M.L.;
Blawert, C.:

Characterisation and corrosion behaviour of plasma electrolytic oxidation coatings on high pressure die cast Mg–5Al–0.4Mn–xCe (x = 0, 0.5, 1) alloys

Characterisation and Corrosion Behaviour of Plasma Electrolytic Oxidation Coatings on High Pressure Die Cast Mg-5Al-0.4Mn-xCe (x=0, 0.5, 1) alloys

Faiz Muhaffel[1], Faruk Mert[2], Huseyin Cimenoglu[1], Daniel Höche[4], Mikhail Zheludkevich[3,4], Carsten Blawert[4,*]

[1]Istanbul Technical University, Metallurgical and Materials Engineering Department, TR-34469, Istanbul, TURKEY

[2]Gazi University, Faculty of Technology, Manufacturing Engineering Department, TR-06500 Ankara, TURKEY

[3]Universidade de Aveiro, DEMAC, CICECO, 3810-193 Aveiro, Portugal

[4]Helmholtz-Zentrum Geesthacht, Magnesium Innovation Centre, Max-Planck-Str. 1, D-21502 Geesthacht, GERMANY

*Corresponding author

Carsten Blawert

Helmholtz-Zentrum Geesthacht, Magnesium Innovation Centre, Max-Planck-Str. 1,

D-21502 Geesthacht, GERMANY

Tel.: + 49 4152 87 1991

Fax: + 49 4152 87 1960

carsten.blawert@hzg.de

Abstract

In the present study, the influence of minor cerium (Ce) additions (up to 1 wt.%) to AM50 magnesium alloy on the plasma electrolytic oxidation (PEO) process and the corrosion performance of the PEO coatings were studied. Therefore, a silicate-based PEO coating was deposited on AM50 containing 0, 0.5 and 1 wt.% Ce under the same processing conditions. The resulting surface morphology, cross-sectional microstructure, phase and chemical compositions of the coatings were determined using scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction analyses (XRD). The corrosion behaviour of the coatings was evaluated by salt spray and electrochemical corrosion tests.

The results show that the growth rate of the coating is reduced, but the thickness is becoming more uniform if cerium is added to AM50 alloy. However, the phase composition and coating morphology are hardly influenced, but the corrosion properties reveal large differences suggesting that the porous PEO coatings have to be considered as a system of coating and substrate. A more uniform corroding substrate such as the cerium alloyed AM50 provides much better protection in combination with a PEO coating than the pure AM50. Flaking-off of large coating areas was observed due to the volume increase caused by corrosion products forming in the interface. Such a severe localised corrosion in the interface causing delamination of the coating can be suppressed by cerium addition.

1. Introduction

Magnesium and its alloys exhibit low density, high specific strength and electromagnetic shielding property, which are very attractive to the automotive, aerospace, electronics and biomedical industries [1–4]. Among miscellaneous commercial magnesium alloys, AM series are commonly used due to their specific properties such as excellent energy absorption and ductility, beside reasonable hardness and strength. However, their relatively poor corrosion resistance in comparison to substituent metals greatly restricts their extended use [1,5–7]. Formation of protective coatings on magnesium alloys is one of the most efficient approaches to increase corrosion resistance of magnesium-based alloys. The widespread coatings are generated by various techniques such as chemical conversion, plasma electrolytic oxidation (PEO), also called micro arc oxidation (MAO), gas-phase deposition, organic compounds deposition, sol-gel, physical vapour deposition (PVD), laser cladding, etc. [8–14]. In recent years, PEO process has been successfully applied to magnesium and its alloys against corrosion owing to low cost, easy preparation, relatively high wear resistance as compared to other coatings [15–17]. Silicate, phosphate and aluminate are common electrolytes for preparation of PEO coatings. The PEO coatings on magnesium alloys are mainly consisted of magnesium oxide (MgO) and some other electrolyte-borne phases (e.g. $Mg_3(PO_4)_2$, Mg_2SiO_4 and $MgAl_2O_4$) according to the used electrolyte type [18–20]. It is a known fact that the PEO coatings prepared in silicate-based electrolytes show superior wear resistance, high hardness and the excellent electromagnetic shielding characteristics of the substrate are maintained [21]. The corrosion behaviour of PEO coatings formed on pure magnesium in different electrolytes was investigated previously [22–24]. Durdu et al. [25] studied the corrosion behaviour of the PEO coatings on commercially pure magnesium developed in the silicate- and phosphate-based electrolytes at different current densities. However, the use of commercially pure magnesium under high load applications is not practical. Therefore, the studies have been mainly focused on the formation of PEO coatings on magnesium alloys and

3

their properties [26–29]. For instance, Liang et al. [30] studied the electrochemical degradation of a silicate- and phosphate-based PEO coating on AM50 magnesium alloy in NaCl solutions with different chloride ion concentrations.

The characteristics of PEO coatings mainly depend on the nature of the substrate metal, applied electrical parameters, composition and concentration of the electrolyte. Concerning the corrosion resistance of magnesium alloys, incorporation of more stable and corrosion-resistant compounds (such as TiO_2, Al_2O_3, SiO_2, ZrO_2 etc.) into the PEO coatings represents an attractive solution [31–35]. However, the bonding and distribution of these particles in the microstructure of the PEO coatings are difficult to control and may not be in desired level which causes loose bonding of the particles, irregular growth and high porosity in the oxide coating. On the other hand, the composition of the substrate acts also as one of the most significant factors in corrosion resistance because the generation of the PEO coating mainly depends on oxidation of the elements from the substrate and their complex phases formed by the chemical reactions with the species from the electrolyte during the oxidation. Hussein et al. [36] investigated the effect of substrate composition of magnesium and magnesium alloys on corrosion behaviour of PEO coatings with respect to alloying elements. They concluded that oxidised AZ91D performed better corrosion resistance that may be attributed to several factors such as discharging behaviour, phase composition, coating structure, thickness and amount of porosity. It is well reported [3] that the alloying elements significantly affect the properties of the magnesium alloys, but also the microstructure and corrosion resistance of PEO coatings can be enhanced on the basis of grain refinement, homogenous micro-arc discharging and improved compactness of the formed coating [37] or the alloy composition [38,39].

The contribution of the rare earth (RE) elements in improving corrosion resistance has been widely studied for magnesium alloys using external sources of cerium, e.g. conversion coatings, sealing processes and incorporation of RE oxides during PEO process [21,40–42].

4

However, another option can be the introduction of Ce from the substrate. Therefore, PEO coating of Ce containing magnesium alloys seems to be an effective way to improve their corrosion resistance, while the presence of Ce in the alloy is also beneficial to microstructure, strength and corrosion resistance of the substrate [43,44]. To our knowledge, a systematic study of the role of minor Ce contents in an AM50 substrate matrix on the microstructure and properties of PEO coatings has not been performed so far. The selected alloys were fully characterised in a previous study [43] showing that the cerium addition improves the corrosion resistance mainly by suppressing localised corrosion attack.

The main aim of the present study was to evaluate how Ce in the substrate affects the PEO processing, how much of Ce from the substrate is incorporated into the PEO coating and how it affects the coating microstructure and the corrosion characteristics of PEO coatings formed on AM50 magnesium alloy with respect to different amounts (up to 1 wt.%) of Ce in the alloy.

2. Experimental

2.1. Materials and processing

Alloy ingots, AM50 (without Ce), AM50Ce0.5 (with 0.5 wt.% Ce) and AM50Ce1 (with 1.0 wt.% Ce) were prepared in an electrical resistance furnace under protective gas. The chemical composition (Table 1) of alloys after high pressure die casting (HPDC) was analysed using a spark emission analyser (SEA), Spectrolab9 from SPECTRO (Kleve, Germany). The alloys were cast into step-shape preheated mould (200 °C) producing plates with four different step thicknesses. More information about alloy manufacturing can be found in the previous study [44]. Specimens used for all investigations were cut from the thickest section of the step plate according to Fig. 1. It is known from HPDC that such step plate specimens have a gradient with higher concentrations at the surface and lower concentrations of the alloying elements in

the centre of such step plates. As a consequence, the actual compositions at the locations where the specimens were taken can be different than the nominal composition so as those at the two sides on each specimen (Tab. 1). There are larger differences (by a factor of two) for the cerium content when the results of the two analysis techniques are compared, but the SEA appears to be the more reliable as it is using a calibration standard. Both results are given, because all of the coating compositions were determined by EDS and one should keep in mind that the Ce content in the coating might be underestimated by a factor of two as well.

The differences on both sides are not that high to expect major differences for the PEO processing, but the corrosion performance can be influenced. The Ce content, especially for the AM50Ce0.5 might be reduced locally below the minimum content required for suppressing pitting corrosion. Normally for most of the specimens, the central side with lower concentration can be identified even without determination of composition by observation of the visible porosity which is higher in the centre of the HPDC plate.

Prior to PEO process, samples with dimensions of Ø 15 x 4 mm were ground using 1200 grit silicon carbide emery papers; rinsed with water, then degreased in ethanol and subsequently dried in air at the room temperature.

2.2. Coating preparation and PEO process

The PEO equipment consisted of a 30 kW pulsed bipolar power supply unit, a stainless steel electrolyte container, an air pump for stirring the electrolyte and an external cooling system. The specimen was connected to the cell as the anode and the stainless steel container served as the cathode. Specimen were subjected to the PEO process with an applied positive voltage of 420 V and a negative voltage of 84 V for 10 min in an electrolyte consisting of 15 g/L sodium metasilicate (Na_2SiO_3, Aldrich) and 2 g/L potassium hydroxide (KOH, Merck). The pulse frequency, positive and negative voltage pulse ratio and duty cycle were 500 Hz, 1:1 and 20%, respectively. During processing, variation of current density and applied voltage

were continuously recorded with a sampling time of 750 ms by using a memory recorder system (Hioki, Memory Hicorder 8808). The temperature of the electrolyte was kept below 25 °C with the aid of the cooling system during PEO process in order to prevent evaporation of the electrolyte and reduce the chemical dissolution of the substrate/coating. After the PEO treatment, the samples were cleaned ultrasonically in ethanol and distilled water, and dried in air at room temperature. According to Ce wt.% content in the alloy, the oxidised samples were referred to as PEO-0, PEO-0.5 and PEO-1.

2.3. Microstructural characterisation of PEO coatings

The surface and cross-section morphologies of the PEO coatings were studied on a scanning electron microscopy (SEM, Zeiss Ultra55) equipped with an energy dispersive X-ray spectrometer (EDS, Oxford). Latter was used to determine the surface composition of the coatings and elemental line-scans across cross sections of the coatings.

X-ray diffraction analyses (XRD) have been performed on a Panalytical system in Bragg-Brentano geometry using Cu-K$_{\alpha 1}$ radiation (wavelength λ=0.15406 nm) at an angle of 2Θ (15-80°) for each sample. Beam spot size was set to be 2x2 mm².

2.4. Corrosion testing

Information about the electrochemical behaviour of the PEO coatings was obtained by performing potentiodynamic polarisation measurements in 0.5% NaCl solution, saturated with atmospheric oxygen. A typical three electrode cell comprising Ag/AgCl (with 3 mol/l KCl) reference, Pt counter and the specimens as working electrodes was used. The exposed surface area of the specimens was 0.5 cm^{2} and the volume of the electrolyte was 330 ml. The dissolution of chloride into deionised water gave a starting pH of 6.5 and the temperature was controlled at 22 ± 0.5 °C while stirring the electrolyte during the experiments. After 30 minutes recording of the free corrosion potential, the polarisation scan was started from –200

mV relative to the free corrosion potential with a scan rate of 0.2 mV/s. The test was terminated when an anodic corrosion current density of 0.1 mA/cm^2 was exceeded.

Additional information about degradation of selected coatings was obtained from electrochemical impedance spectroscopy (EIS) measurements performed in the same electrolyte using the same cell as described above for the polarisation measurements. The latter tests were carried out at an open circuit potential in the frequency range of 0.01 to 30,000 Hz using amplitudes of ± 10 mV rms. Fitting of spectra was performed using ZView software and the equivalent circuits introduced in the result section. The goodness of fit of the simulated spectra corresponded to chi-squared (square of the standard deviation between the original data and the calculated spectrum) values was less than 0.01. The errors for the individual parameters of the equivalent electrical circuits (such as **CPE** and **R**) were less than 6%.

Salt spray corrosion tests were performed according to DIN EN ISO 9227 [27] using 5% NaCl for a total time of 72 hours (3 days) in a WEISS SC400 salt spray test chamber (Reiskirchen, Germany). The corrosion attack was observed optically on three specimens for each treatment with a stereo microscope at about 20x magnification. The total number of defects was counted and classified according to size (small <1 mm and large >1 mm) and location on the specimen (main circular area/ edges/ cylindrical circumference).

3. Results

3.1. PEO processing

The processing was performed in constant voltage mode which means that the ramp-up to the treatment voltage was relatively quick (about 40 s) and there was no major difference noticed in the voltage trace between the three different substrates. However the current density during the treatment and also the maximum peak current density as well as the final current density

at the end of the treatment (Fig. 2) depend obviously on the substrate composition. The current for the pure AM50 was always higher suggesting that more magnesium is converted during the processing and that the coating growth might be faster assuming that the cathodic side reactions are the same if the experimental set-up and electrolyte remain the same. Furthermore this indicates that the effective coating resistance without cerium in the substrate is smaller, thus the same driving force (applied voltage) causes a higher current.

3.2. Surface and cross-sectional morphologies of PEO coatings

A weak influence of the substrate composition is visible in the surface morphology of the produced coatings. Interestingly there is an increasing number of small pimples on the surface with increasing amount of cerium in the substrate material (Fig. 3) which might be related to the phases (e.g. $Al_{11}Ce_3$) that are more resistant either chemically, against dissolution in the electrolyte, and/or thermally, against melting and evaporation in PEO discharges. Apart from that the morphology of the three coatings regarding number and size of pores which are visible on the surface is similar.

However, the cross sections of the three coatings reveal hardly any differences in the coating morphology (Fig. 4). The build-up of the coatings is very similar, consisting of a thin interface layer between coating and substrate, followed by a pore band close to the interface and a thick top layer. The latter is not dense and shows a larger number of through-going open pores resulting from the discharges leaving behind discharge channels reaching from the surface towards the pore band close to the interface; thus the electrolyte can penetrate easily and quickly through the coating. Additionally, closed pores are visible, most likely formed by gas entrapment during solidification of melted regions around the discharge channels. The coating thickness is slightly higher for the AM50 (25 ± 5 µm) compared to about 20 ± 2 µm for the two cerium containing substrates which correspond to the observed higher current

density during PEO treatment. However, the coating growth on the AM50 substrate is less uniform and the interface is waved indicating locally enhanced dissolution and/or deposition.

3.2. Phase and elemental compositions

Phase analysis shown in Fig. 5 revealed the presence of crystalline Mg_2SiO_4 (forsterite) and MgO (periclase) within the PEO coating. The bulk substrate magnesium α- phase was measured to be constant for all three conditions suggesting that the X-ray penetrate the coating and that coating thickness is in the same range for the three substrates. Other silicate phases like $MgSiO_3$ (enstatite) were not present. The observations indicate a negligible influence of low amount Ce additions to the Mg alloy on the PEO coating phase formation. Furthermore, Ce containing secondary phases in the substrate could not be detected. According to our previous study, the substrate contains β-phase ($Mg_{17}Al_{12}$) for the pure AM50 and additional $Al_{11}Ce_3$ phase for the two alloys with cerium addition reducing the amount of β-phase [43]. Due to the detection limit (based on tiny volume fraction) and the overlapping of the PEO coating diffraction pattern their existence cannot be validated here.

The surface composition of the coating is nearly the same for all three substrates and due to dissolution effects the small substrate differences on the two sides of a specimen are not detectable anymore (Tab. 2). Cerium is, if at all, only present in traces thus an influence on the properties or the phase composition can be neglected, which is consistent with the XRD results. However, the concentration of the main elements forming the coating in the atomic ratio (Mg:Si:O = 17:15:60) is not in the right balance for a coating consisting only of MgO and Mg_2SiO_4. Especially the amount of Mg is too low and a possible explanation might be the different depth from which the information is obtained by XRD (penetrating the coating) and EDS (< 4 µm). Some of the Si detected on the surface might be still present in the form of Na_2SiO_3 or in an amorphous state not detected by the XRD.

The elemental line scans performed by EDS (Fig. 6) show an even enhanced depletion of oxygen (30 wt.%) in the bulk of the coating while the other two main elements (Si: 25 wt.% and Mg: 30 wt.%) show an increasing amount compared to the surface composition. The other elements of the alloy (Al, Mn and Ce) are still present in the coating, but they are too much diluted to give reasonable signal, thus only the main elements are depicted to demonstrate that the composition of the coatings are similar independent from the substrate material. The coating on AM50 (< 25 µm) is slightly thicker than the two coatings on the cerium containing substrates (< 20 µm), which is consistent with the cross section observations. Furthermore, close to the interface the content of Mg seems to increase compared to the content of Si.

Distribution uniformity of the main elements (Mg, Si, O, Al, Ce) was also checked qualitatively by EDS elemental mapping shown in Fig. 7. The distribution suggests that the coatings are relatively uniform in the composition (except for the decrease of Si towards the interface and vice versa the increase of Mg) and also the minor alloying elements are uniformly distributed in the coating. Enrichments are mainly visible in the substrate due to casting segregation and precipitates.

3.3. Corrosion

3.3.1. Salt spray corrosion results

Due to the fact that the weight loss measurements are not applicable for oxide based PEO coatings (chromic acid cleaning would also remove the coating and not only the corrosion products) the evaluation was done optically and the results are summarised in Tab. 3). One can clearly see that the addition of cerium to the alloy is decreasing the size and number of the defects in the coatings. As the structure and composition of the coating is almost unchanged by the small amounts of cerium addition, this effect has to be correlated with the substrate performance. The latter is consistent with the observation for the uncoated alloys, that the

addition of cerium is reducing the occurrence of severe localised corrosion [43], but one can realise that the performance of the two main sides on the same specimen can be different. This might be related to the distribution of alloying elements in the HPDC process and how the specimens were taken from the step plate, having a high and low concentration side for Al and RE elements. Basically, one side shows no defects while the other contributes to the total amount of defects given in Tab. 3. Considering the composition of the two sides on the different substrates (Tab. 1) the occurrence of defects is obviously related to the cerium content in the substrate. If it is below or around 0.5 wt.% cerium the chance of visible defect formation increases. The typical appearance of the defects on selected specimen for each substrate is shown in Fig. 8. The PEO coatings are not dense and a certain number of open through-going pores exist in the coating, thus the electrolyte can reach quickly the interface region which is just covered by a thin (about 1 µm) dense oxide based film. This film is attacked by the electrolyte and slowly starts to dissolve/break down and at weak points magnesium corrosion can start after a certain incubation period. If enough corrosion products were formed the relative brittle coating near the defect is lifted off by the volume increase of Mg corrosion products in the interface region. In the defect regions the coating is completely removed and the bare magnesium alloy is visible. Interestingly the defect formation is not related to the internal porosity of high pressure die cast material. Obviously the PEO process is able to form the protective coating also in the inner part of open pores, thus they are not the weak points of the coatings. For example the selected PEO_0.5 specimen has large pores but no indication of corrosion around them (Fig. 8b).

3.3.2 Potentiodynamic polarisation

The polarisation results seems to confirm clearly the salt spray results that there are two sides on the HPDC specimens with different corrosion performance (Fig. 9). However, differences in the alloying element concentration on the two sides are most likely not the explanation for

the observed polarisation results. There is a clear difference in the corrosion and failure mechanisms between salt spray and polarisation. Salt spray as a "long term" test (72 hours) reveals flaking off of larger coating areas obviously due to accumulation of corrosion products while there are no visible coating defects observed in the "short term" polarisation tests (1 h). Consequently, different mechanisms must be acting in short exposure time under external polarisation. In the case of short term polarisation, it is much more likely that the results are related to the open porosity, namely the number and size of the open pores, rather than to the composition of the substrate. The coating material is relatively stable against dissolution if the specimen is polarised and the measured current should be mainly a result of substrate dissolution at the weak points (open pores) of the coating. Therefore, polarisation current can be considered as a measure of open porosity indicating the sum of weak points in the coating which may act as starting points for a corrosion attack but does not give reliable prediction of the long term behaviour. Occurrence of open porosity in the coating depends somehow on the processing parameters and the microstructure but a straight correlation seems to be impossible. The pores and their size appear to have a statistical distribution similar to distribution of the discharges on the surface which are producing the open pores. Thus, coming back to the polarisation results, they indicate strong variations between coatings produced on the same substrate and even between the two sides on one specimen. These large variations in corrosion properties are visible in Fig. 9. Thus comparing coatings on different substrates regarding substrate influence on properties is not reasonable. They cannot be correlated to any microstructural features (size and number of pores, composition and thickness) of the substrate and coating because those differences are relatively small compared to the large differences in corrosion performance expressed by the corrosion current. However, open porosity in PEO processing is well known and its statistical distribution seems to be the only explanation possible for the observed variations. There are specimens with larger areas free of defects and some regions having one or even more open

pores in the area selected for corrosion measurements. Therefore, somehow polarisation is an indicator of starting coating quality, detecting open pores, but the long term behaviour is controlled by additional features.

3.3.3. Results of EIS

The EIS measurements were performed to study the degradation process during immersion in 0.5% NaCl solution for the two selected coatings produced under the same processing conditions on substrates representing a substrate which tends to pitting corrosion (AM50) and one which tends to passive film formation (AM50+1Ce), in long term corrosion exposure studies [43]. This selection should be suitable to understand the substrate effects on the long term behaviour of the coating. It should be noted that the internal porosity of the material appears to be of no major concern for the corrosion resistance. Substrates with open pores can be treated by the PEO process [45] and the corrosion resistance appears to be in the same order compared to the coating on a flat surface. Fig. 10 shows a typical coated open pore demonstrating that the performance is sufficient to prevent corrosion suggesting that the pores can be coated in the same manner as the rest of the surface.

Thus, the first example (Fig. 11a) shows the performance of a coating on a specimen containing only Al (AM50, outer region) while the second example (Fig. 11b) shows the same for a coating on a surface enriched in Al and RE elements (AM50+1Ce, outer region). The evolution of impedance spectra was analysed by numerical fitting of the recorded Bode plots using the equivalent circuit models given in Fig. 12 and the results in the form of calculated resistance values are given in Fig. 13.

The models consider the microstructural features of the coatings and the observed corrosion morphology during and after the exposure to the electrolyte. The constant phase elements where introduced instead of capacitances in order to account for non-uniform distribution of

thickness and dielectric properties of the respective layers. Both coatings consist of an outer porous layer (represented by its resistance R_o and the corresponding CPE_o) and a thin inner dense interface layer (represented by its resistance R_i and the corresponding CPE_i). Porosity and thickness of the coatings are similar regardless of the substrate on which they were produced. The performance of the two specimens is similar although the AM50 seems to degrade slightly faster (Fig. 14). During immersion, the resistance of the outer layer is continuously degrading and after a relatively short time (10 h) it is lost. The respective time constant is not detectable any more on the respective spectra. This process might be related to the diffusion and penetration of the electrolyte towards the inner layer, dissolution of phases, widening of the pores and electrolyte alkalisation in there. Thickness, composition and porosity are the main parameters for the outer layer and as they are very similar for the two coatings the protective performance is comparable. However, the EIS spectra suggest that the contact of electrolyte with the inner layer occurs very soon (1h) and resistance of the outer and inner layer start to decrease already between the first measurement after 5 min and the second one after 1h. After 4 hours, an additional relaxation process is already visible at low frequencies. The respective third time constant can be introduced to the equivalent circuit to describe these processes which can be asigned to the local breakdown of the interface layer and formation of an electrochemical double layer and a related polarisation resistance (R_p and CPE_{dl}). At this time, the role of the substrate composition becomes important and differences in the performance arise. The AM50 specimen shows a continious degradation of outer and inner layers with parallel increase in corrosion activity. At certain time the polarisation resistance stabilises at a relatively low value. The stabilisation of this parameter is most probably related to the effect of diffusion limitations which affect the polarisation resistance. For the AM50 alloy, the protective function of the inner layer is also lost after 72 hours of immersion and severe pitting occurs which finally results in flaking off of large coating areas. Fig. 15 shows a typical appearance of the specimens at the end of the test, after 144 hours. In

contrast the inner layer and the polarisation resistance on the AM50Ce1 alloy stabilises at much higher resistance values. In this case only small areas show the loss of the outer top layer at 144 hours and in the impedance spectra relatively high and stable polarisation resistance values are observed. There is also no evidence that diffusion processes start dominating confirming suggestion that there is no active Mg dissolution. This indicates that either the original inner layer still exists or that it is slowly replaced by a new stable conversion film. However, the corrosion behaviour is relatively stable after 96 hours, without indication of further loss of corrosion resistance which remains about 10 times higher compared to the AM50 alloy. This observation correlates very well with the performance and failure in the salt spray test of different coated substrates even though the test conditions were dissimilar, but there is much more similarity between the two long term salt spray and impedance tests than between impedance and potentiodynamic polarisation tests. The latter can be better correlated to the initial performance of a coating but not to the long term performance.

4. Discussion

The microstructural characterisation of the coatings reveal that the main phases formed in the coating (MgO and Mg_2SiO_4) are not influenced by the cerium additions. The phase composition and distribution within the coatings as well as the elemental distribution of the main elements forming the coatings are nearly the same for all three coatings. Also the coating morphology including porosity (size, shape and distribution) show no visible change even if a small effect with increasing number small pimples on the surface is visible. Later has obviously no effect on the surface layer properties. Furthermore, there is neither evidence for enrichment of cerium in the coating nor new cerium rich phases are detected. In contrast, the amount of cerium in the coating seems to be even slightly diluted (0.05 wt% for both coatings produced on the cerium containing substrates) considering the fact that about 1/5 of the

coating composition is coming from the original substrate (20 wt.% magnesium in the coating) suggesting 0.1 or 0.2 wt.% cerium respectively if cerium would be incorporated into the coating in the same manner as magnesium. Consequently, the influence of small additions of cerium on the morphology of PEO coatings can be neglected.

Nevertheless, these small amounts of cerium do have obviously an influence on the anodising behaviour of the substrate alloys. While applying the same voltage as the driving force for the anodisation process the current response of the substrates is different. The pure AM50 shows throughout the whole PEO process a higher current density compared to the cerium alloyed materials indicating that the barrier properties of the forming films/coatings on the various substrates are different. The performance of the two cerium containing versions is similar, but the one with higher cerium content has a slightly lower current density throughout the process. The thicker coating produced on AM50 correlates quite well with the higher current density suggesting that the current driven dissolution of substrate material and subsequent deposition of Mg rich compounds with low solubility are essential steps in the coating formation. However, the current study can give no answer to the question if the reason for the lower current density in the presence of cerium is caused by the better resistance against dissolution of the alloy itself or if more stable conversion products in the interface do reduce the current by increasing the resistance. The current during PEO of the cerium containing substrates remain lower throughout the whole treatment sequence although all coatings show the expected decrease in the current with treatment time related to increasing top coat thickness (resistance) approximately following the Ohm's law. However, the porous structure of the coatings which is a result of discharges sealing the old discharge channels but forming the new ones at the same time, continuously offers path ways for the treatment solution to directly reach the substrate. This process inherent mechanism is obviously preventing the formation of a dense coating suppressing the current flow completely. At the bottom of the open pores (discharge channels) only a thin film can be formed by conversion products and its

ability to reduce the current is limited by its small thickness. However, the lower final current in the presence of cerium seems to indicate that it may have a positive effect on the resistance of this thin film. Nevertheless, these through-going pores are the weak points of the coating in terms of corrosion resistance which is consistent with the findings of Song et al. [39] although we see a different degradation mechanism for our type of coatings (Fig. 16).

The open pores in the coating are the reason why the substrate material plays an important role in the degradation behaviour of PEO coatings. The pores offer pathways not only for the electrolyte to reach the substrate – coating interface but also to transport soluble corrosion products outside. If the formation of the corrosion products on the substrate is faster than the transport outside, they might be deposited in the pores and at the interface. The latter depends on the solubility limit of the corrosion products in the corrosive surrounding and can have a positive effect on the corrosion resistance of the coating if pores are sealed or deposits are strengthening the interface layer. However, to obtain this positive effect, it is important to control the dissolution rate of the substrate. If this is not possible the volume increase of the corrosion products can become so large that the resulting stresses causes cracking and flacking-off of coating areas. On the one side, the coating microstructure (pore sizes and distribution) and maybe also the mechanical properties are controlling the available volume and tendency to crack, but the substrate is even more important because it provides the corrosion products which are the source of the stresses.

Therefore, it is important to follow the same guidelines for the substrate selection for PEO treatments as for the selection of a corrosion resistant magnesium alloy. It is necessary to control the heavy metal impurities and to optimise the alloy resistance by the proper choice and amount of alloying elements. The performance of AM50 is reasonably good, but the amount of Al should not be reduced any further, which becomes obvious from the corrosion performance of the central sides of the specimens (coated or not). Furthermore, as previously shown [43], cerium can reduce the amount of pitting corrosion of the AM50 alloy. For this, a

certain limit of Al as well as Ce is required, because the $Al_{11}Ce_3$ phase can replace the obviously more active ß-phase and can include impurities in its structure. Both help to reduce the tendency to pitting corrosion and only if this strong localised corrosion occurs at the interface it can damage the coating because the volume increase of the corrosion products would cause stresses and lead to flaking-off of large coating areas. A certain amount of cerium seems to be necessary to suppress the pitting corrosion attack. Looking at the results on the different surfaces and the surface compositions, this limit seems to be around 0.5 wt.% cerium. In that way, the cerium addition helps to increase the long-term performance of the coatings.

Regarding the corrosion testing, potentiodynamic polarisation measurements appear to be not suitable to distinguish between minor substrate influences on the corrosion performance of the coatings because the short term results are dominated by open porosity which is not depending on the composition of the substrate but on the PEO processing parameters. To see the effect of substrate, long-term tests are required (e.g. salt spray or EIS), consistent with our previous studies [43] demonstrating that the substrate performance is similar in the beginning and it requires about 24 hours before pitting starts on the AM50 while the presence of Ce can retard the pitting even after 336 hours. The pitting as a substrate property in combination with excessive volume increase due to corrosion product formation causing flaking-off of coatings areas was identified as the main failure mechanism of the coatings in the both long-term tests. All tests which are running shorter than 24 hours fail to detect major differences between the coatings (e.g. see Fig. 13 – EIS resistance as function of time). The polarisation measurements (neglecting the strong variations) are able to predict the starting resistance values for EIS but not the long-term behaviour.

5. Conclusions

19

The experimental results indicate that even minor additions of alloying elements can have an influence on the PEO processing and corrosion properties of PEO coated AM50 magnesium alloy. The observed inherent open porosity of HPDC magnesium alloys is no concern in PEO processing.

Under similar constant voltage processing conditions the average coating growth rate (2.5 µm/min) is higher for AM50 compared to the alloys containing up to 1 wt% cerium (2 µm/min), but the variation in coating thickness is also increasing. AM50 is less stable from the corrosion point of view and should have higher dissolution rates compared to the alloys with cerium, suggesting that the coating formation during PEO depends partly on a conversion step involving the reaction of dissolved Mg with electrolyte components and the subsequent deposition of those reaction products on the surface if their solubility limit is exceeded. However, the phase composition and porosity of the coatings are hardly affected by the minor alloying additions of cerium.

The coating corrosion resistance and degradation behaviour depend strongly on the substrate material and its own inherent corrosion resistance as the electrolyte can easily penetrate the outer layer of the PEO coatings. Failure of the coating is often a consequence of volume increase due to the formation of corrosion products in the interface which create stresses in the PEO film, lifting it of the surface and finally resulting in flaking-off of larger coating areas. Thus a substrate with a tendency for a mild uniform corrosion is performing better than that which tends to exhibit localised corrosion. Thus corrosion resistance of PEO-coated Mg alloys can be improved by the addition of alloying elements to the substrate material. The selected element should help to reduce localised pitting and form passive films promoting stable uniform corrosion. Cerium is such an element for the alloy AM50, which improves the corrosion performance of the alloy and thus prevent early failure of the coating deposited on top of it.

Finally, substrate and PEO coating are a system and both need consideration if the corrosion performance of the coated alloy should be optimised.

References

[1] M. Easton, A. Beer, M. Barnett, C. Davies, G. Dunlop, Y. Durandet, et al., Magnesium alloy applications in automotive structures, Jom. 60 (2008) 57–62.

[2] K. Funatani, Emerging technology in surface modification of light metals, Surf. Coatings Technol. 133-134 (2000) 264–272.

[3] G.L. Makar, J. Kruger, Corrosion of magnesium, Int. Mater. Rev. 38 (1993) 138–153.

[4] S. Shadanbaz, G.J. Dias, Calcium phosphate coatings on magnesium alloys for biomedical applications: a review., Acta Biomater. 8 (2012) 20–30.

[5] H.E. Friedrich, B.L. Mordike, Magnesium Technology - Metallurgy, Design Data, Applications, Springer-Verlag, Berlin Heidelberg, 2006.

[6] M.K. Kulekci, Magnesium and its alloys applications in automotive industry, Int. J. Adv. Manuf. Technol. 39 (2007) 851–865.

[7] G. Song, A. Atrens, Corrosion mechanisms of magnesium alloys, Adv. Eng. Mater. (1999) 11–33.

[8] Y.W. Song, D.Y. Shan, E.H. Han, High corrosion resistance of electroless composite plating coatings on AZ91D magnesium alloys, Electrochim. Acta. 53 (2008) 2135–2143.

[9] R.F. Zhang, D.Y. Shan, R.S. Chen, E.H. Han, Effects of electric parameters on properties of anodic coatings formed on magnesium alloys, Mater. Chem. Phys. 107 (2008) 356–363.

[10] Y. Song, D. Shan, R. Chen, F. Zhang, E.-H. Han, A novel phosphate conversion film on Mg–8.8Li alloy, Surf. Coatings Technol. 203 (2009) 1107–1113.

[11]   H. Meifeng, L. Lei, W. Yating, T. Zhixin, H. Wenbin, Corrosion properties of surface-modified AZ91D magnesium alloy, Corros. Sci. 50 (2008) 3267–3273.

[12]   T. Lei, C. Ouyang, W. Tang, L.-F. Li, L.-S. Zhou, Preparation of MgO coatings on magnesium alloys for corrosion protection, Surf. Coatings Technol. 204 (2010) 3798–3803.

[13]   P. Liu, X. Pan, W. Yang, K. Cai, Y. Chen, Improved anticorrosion of magnesium alloy via layer-by-layer self-assembly technique combined with micro-arc oxidation, Mater. Lett. 75 (2012) 118–121.

[14]   Y. Song, K. Dong, D. Shan, E.-H. Han, Investigation of a novel self-sealing pore micro-arc oxidation film on AM60 magnesium alloy, J. Magnes. Alloy. 1 (2013) 82–87.

[15]   R. Arrabal, E. Matykina, T. Hashimoto, P. Skeldon, G.E. Thompson, Characterization of AC PEO coatings on magnesium alloys, Surf. Coatings Technol. 203 (2009) 2207–2220.

[16]   Q. Cai, L. Wang, B. Wei, Q. Liu, Electrochemical performance of microarc oxidation films formed on AZ91D magnesium alloy in silicate and phosphate electrolytes, Surf. Coatings Technol. 200 (2006) 3727–3733.

[17]   H. Guo, M. An, S. Xu, H. Huo, Microarc oxidation of corrosion resistant ceramic coating on a magnesium alloy, Mater. Lett. 60 (2006) 1538–1541.

[18]   H.F. Guo, M.Z. An, H.B. Huo, S. Xu, L.J. Wu, Microstructure characteristic of ceramic coatings fabricated on magnesium alloys by micro-arc oxidation in alkaline silicate solutions, Appl. Surf. Sci. 252 (2006) 7911–7916.

[19]   Y. Ma, H. Hu, D. Northwood, X. Nie, Optimization of the electrolytic plasma oxidation processes for corrosion protection of magnesium alloy AM50 using the Taguchi method, J. Mater. Process. Technol. 182 (2007) 58–64.

[20]   A. Ghasemi, V.S. Raja, C. Blawert, W. Dietzel, K.U. Kainer, Study of the structure and corrosion behavior of PEO coatings on AM50 magnesium alloy by electrochemical impedance spectroscopy, Surf. Coatings Technol. 202 (2008) 3513–3518.

[21]   F. Liu, Y. Li, J. Gu, Q. Yan, Q. Luo, Q. Cai, Preparation and performance of coating on rare-earth compounds-immersed magnesium alloy by micro-arc oxidation, Trans. Nonferrous Met. Soc. China. 22 (2012) 1647–1654.

[22]   P. Shi, W.F. Ng, M.H. Wong, F.T. Cheng, Improvement of corrosion resistance of pure magnesium in Hanks' solution by microarc oxidation with sol–gel TiO_2 sealing, J. Alloys Compd. 469 (2009) 286–292.

[23]   W. Mu, Y. Han, Characterization and properties of the MgF_2/ZrO_2 composite coatings on magnesium prepared by micro-arc oxidation, Surf. Coatings Technol. 202 (2008) 4278–4284.

[24] H. Yun, F. Gao, S. Durdu, A. Polat, M. Usta, A.H. Ucisik, et al., Evaluation of micro arc oxidized coatings on pure magnesium, Front. Appl. Plasma Technol. 3 (2010) 40–44.

[25] S. Durdu, A. Aytaç, M. Usta, Characterization and corrosion behavior of ceramic coating on magnesium by micro-arc oxidation, J. Alloys Compd. 509 (2011) 8601–8606.

[26] P. Bala Srinivasan, J. Liang, C. Blawert, M. Störmer, W. Dietzel, Effect of current density on the microstructure and corrosion behaviour of plasma electrolytic oxidation treated AM50 magnesium alloy, Appl. Surf. Sci. 255 (2009) 4212–4218.

[27] G. Rapheal, S. Kumar, C. Blawert, N.B. Dahotre, Wear behavior of plasma electrolytic oxidation (PEO) and hybrid coatings of PEO and laser on MRI 230D magnesium alloy, Wear. 271 (2011) 1987–1997.

[28] J. Liang, L. Hu, J. Hao, Characterization of microarc oxidation coatings formed on AM60B magnesium alloy in silicate and phosphate electrolytes, Appl. Surf. Sci. 253 (2007) 4490–4496.

[29] C. Ma, M. Zhang, Y. Yuan, X. Jing, X. Bai, Tribological behavior of plasma electrolytic oxidation coatings on the surface of Mg–8Li–1Al alloy, Tribol. Int. 47 (2012) 62–68.

[30] J. Liang, P.B. Srinivasan, C. Blawert, W. Dietzel, Influence of chloride ion concentration on the electrochemical corrosion behaviour of plasma electrolytic oxidation coated AM50 magnesium alloy, Electrochim. Acta. 55 (2010) 6802–6811.

[31] J. Liang, L. Hu, J. Hao, Preparation and characterization of oxide films containing crystalline TiO_2 on magnesium alloy by plasma electrolytic oxidation, Electrochim. Acta. 52 (2007) 4836–4840.

[32] R. Arrabal, E. Matykina, P. Skeldon, G.E. Thompson, Incorporation of zirconia particles into coatings formed on magnesium by plasma electrolytic oxidation, J. Mater. Sci. 43 (2008) 1532–1538.

[33] J. Liang, P.B. Srinivasan, C. Blawert, W. Dietzel, Comparison of electrochemical corrosion behaviour of MgO and ZrO_2 coatings on AM50 magnesium alloy formed by plasma electrolytic oxidation, Corros. Sci. 51 (2009) 2483–2492.

[34] M. Laleh, a. S. Rouhaghdam, T. Shahrabi, a. Shanghi, Effect of alumina sol addition to micro-arc oxidation electrolyte on the properties of MAO coatings formed on magnesium alloy AZ91D, J. Alloys Compd. 496 (2010) 548–552.

[35] W. Li, L. Zhu, H. Liu, Effects of silicate concentration on anodic films formed on AZ91D magnesium alloy in solution containing silica sol, Surf. Coatings Technol. 201 (2006) 2505–2511.

[36] R.O. Hussein, D.O. Northwood, X. Nie, The effect of processing parameters and substrate composition on the corrosion resistance of plasma electrolytic oxidation (PEO) coated magnesium alloys, Surf. Coatings Technol. 237 (2013) 357–368.

[37] J. Jiang, Q. Zhou, J. Yu, A. Ma, D. Song, F. Lu, et al., Comparative analysis for corrosion resistance of micro-arc oxidation coatings on coarse-grained and ultra-fine grained AZ91D Mg alloy, Surf. Coatings Technol. 216 (2013) 259–266.

[38] Z. Shi, The corrosion performance of anodized magnesium alloys, PhD thesis, University of Queensland, 2005.

[39] G. Song, Z. Shi, Corrosion mechanism and evaluation of anodized magnesium alloys, Corros. Sci. 85 (2014) 126–140.

[40] M. Laleh, F. Kargar, a. S. Rouhaghdam, Investigation of rare earth sealing of porous micro-arc oxidation coating formed on AZ91D magnesium alloy, J. Rare Earths. 30 (2012) 1293–1297.

[41] D. Chen, J. Wu, Y. Liang, S. Ye, W. Li, Preparation of cerium oxide based environment-friendly chemical conversion coating on magnesium alloy with additives, Trans. Nonferrous Met. Soc. China. 21 (2011) 1905–1910.

[42] T.S. Lim, H.S. Ryu, S.-H. Hong, Electrochemical corrosion properties of CeO_2-containing coatings on AZ31 magnesium alloys prepared by plasma electrolytic oxidation, Corros. Sci. 62 (2012) 104–111.

[43] F. Mert, C. Blawert, K.U. Kainer, N. Hort, Influence of cerium additions on the corrosion behaviour of high pressure die cast AM50 alloy, Corros. Sci. 65 (2012) 145–151.

[44] F. Mert, A. Özdemir, K.U. Kainer, N. Hort, Influence of Ce addition on microstructure and mechanical properties of high pressure die cast AM50 magnesium alloy, Trans. Nonferrous Met. Soc. China. 23 (2013) 66–72.

[45] T. Abdulla, A. Yerokhin, R. Goodall, Effect of Plasma Electrolytic Oxidation coating on the specific strength of open-cell aluminium foams, Materials & Design 32, 7 (2011) 3742-3749.