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Blawert, C.; Heitmann, V.; Dietzel, W.; Nykyforchyn, H.M.; Klapkiv, M.D.:

Influence of electrolyte on corrosion properties of plasma electrolytic conversion coated magnesium alloys

Influence of electrolyte on corrosion properties of plasma electrolytic conversion coated magnesium alloys

C. Blawert, V. Heitmann and W. Dietzel
Centre for Magnesium Technology, GKSS-Forschungszentrum Geesthacht GmbH,
Max-Planck-Str. 1, 21502 Geesthacht, Germany

H. M. Nykyforchyn and M. D. Klapkiv
Karpenko Physico-Mechanical Institute of the National Academy of Sciences of Ukraine,
Lviv, Ukraine

Abstract

The synthesis of oxides in a low-temperature electrolytic plasma allows to cover surfaces of magnesium and its alloys with multifunctional protective oxide-ceramic coatings. The corrosion properties of these layers are strongly dependent on their porosity. In order to minimize the porosity and to optimize the corrosion properties of the layers, the electrolyte concentration and composition (addition of CrO_3 as corrosion inhibitor) were varied, and the influences on layer structure, composition, and properties with a main focus on corrosion behaviour were studied.

The corrosion properties of various layers thus generated were studied in 5% NaCl solution by measuring electrochemical polarization curves and by electrochemical impedance spectroscopy (EIS) at pH 3 and 6. Using XRD, LM, SEM and EDX to evaluate the composition and microstructure of the modified surfaces, the corrosion results were related to the microstructure and composition of the specific layer. The better results were obtained for layers produced at higher electrolyte concentration, whereas the addition of CrO_3 had no significant beneficial effect.

Corresponding Author: Carsten Blawert
GKSS-Forschungszentrum Geesthacht GmbH
Max-Planck-Str. 1, 21502 Geesthacht, Germany
email: carsten.blawert@gkss.de
fax: +49 4152 87 2620
ph: +49 4152 87 2625

1. Introduction

The anodic behaviour of magnesium and magnesium alloys is strongly influenced by the voltage applied. Generally, different passive and active states were found varying with the applied voltage but also with alloy and electrolyte composition. Certain electrolytes, including aluminate and tetraborate, contribute to film thickness and structure, whereas other electrolytes such as fluoride and phosphate influence the film colour, opacity, and the uniformity of finish. Control of the sparking process, inherent in Mg anodizing, is also affected by bath components that do not otherwise contribute to the Mg anodized coating [1-3]. Furthermore, the composition of the anodized layer strongly depends on the composition of the electrolyte and on the composition of the substrate, as alloying elements show enrichment in the layer [4-6].

Several sources describe the structure of the ceramic coatings on magnesium as a two-layer or three-layer system. Adjacent to the substrate is a very thin layer, above this is a moderately porous layer while the outer layer is much more porous. Two options exist of how to make use of this porosity. The outer layer can be impregnated, or it can be grinded away in order to expose the harder and denser underlying layer [7].

A clear influence exists of the process parameters, the electrolyte composition and the substrate on the corrosion properties [2, 3, 8]. Our previous work has shown that the corrosion behaviour is strongly related to the open porosity [9]. Therefore, it is an objective to reduce the porosity and/or to identify other mechanisms for optimizing the corrosion resistance. The present study concentrates on two possible approaches for improving the corrosion resistance: Firstly, the concentration of the standard electrolyte (used in our previous studies [9, 10]) was raised, and secondly a corrosion inhibitor was incorporated into the coating. As a first scientific approach we have chosen hexavalent chromium as a well known corrosion inhibitor for magnesium alloys. However, we were well aware of the fact that this substance should be replaced by other, more experimental and environmental friendly inhibitors for magnesium, if it should turn out that an inhibitor can be successfully incorporated into a PEO coating without loosing its inhibiting function.

2. Experimental details

Oxide ceramic coatings were produced on specimen plates (100 x 15 x 3 mm) of a magnesium alloy designated BMD10 (0.8% Zn, 7.1-7.9% Y, 0.63% Cd, 0.5% Zr, remainder Mg) which were immersed in three different electrolytes containing mainly potassium hydroxide and sodium silicate. Compared to the first standard electrolyte (low concentration), which was used in our previous studies [9, 10] the concentration of the second electrolyte was increased. The third electrolyte was obtained by adding CrO_3 as a corrosion inhibitor to the high concentration electrolyte. The compositions of the three electrolytes are given in Table 1. The synthesis of the oxide ceramic layer was performed under a cathodic to anodic current density ratios of one (Ic/Ia = 1) at 10 A/dm^2. Details of the process are given elsewhere [10]. The treatment times were 15 minutes, resulting in different layer thicknesses depending on the electrolyte. After the treatment, the specimens were boiled in distilled water for 30 minutes to remove remains of the treatment electrolyte and to form $Mg(OH)_2$ on the bottom of the pores in order to increase the corrosion resistance.

Electrolyte composition	KOH (g/l)	water glass (g/l)	CrO_3 (g/l)
Standard	3	2	-
High concentration	10	15	-
High concentration + CrO_3	10	15	0.1

Tab 1: Composition of the electrolytes

The surface appearance of each surface layer was investigated by optical (LM) and scanning electron microscopy (SEM). The total pore density was calculated from overview pictures taken at 100 x magnification. The open pore (defect) density was counted after reaction marking of the defects in an electrolyte containing 60 g/l CH_3COOH + 5 g/l $CuSO_4 \cdot 5H_2O$ + 15 g/l $ZnCl_2 \cdot 7H_2O$. X-ray diffraction with Cu K_α radiation was used to determine the phases present in the layers, and EDX was used to determine the elemental composition of the layers.

The corrosion properties of the various layers were studied in electrochemical polarisation measurements performed in aqueous 5% NaCl solutions saturated with atmospheric oxygen and adjusted by HCl to pH 3 and 6, respectively. In addition, electrochemical impedance spectroscopy (EIS) was performed after various times of immersion to follow the change in the corrosion behaviour as a function of immersion time. The corrosion cell (333 ml) with a three electrode set-up consisted of a Ag/AgCl reference electrode, a Pt counter electrode and the PEO coated specimen as the working electrode. The electrolyte temperature was controlled to 22 ± 0.5°C, the electrolyte was stirred during the experiments. One experiment consisted of 23 subsequent tests and the total test period was about 24 hours, i.e.:

1) 30 minutes recording of the free corrosion potential.

2) Potentiodynamic polarization scan starting from –200 mV relative to the free corrosion potential at a scan rate of 0.2 mV/s. To minimize the damage on the specimen surface the test was terminated when a corrosion current of 0.1 mA was exceeded before the next sequence started. The corrosion rate was calculated from the current density determined at the intersection of the Tafel slope of the cathodic branch of the polarization curve with the vertical line through the corrosion potential.

3-22) Electrochemical impedance measurements at free corrosion potential using a Gill AC over the frequency range from 10 kHz to 0.01 Hz. The amplitude of the sinusoidal signals was 10 mV. The measurements were repeated every hour. Because of unstable conditions at the low frequencies the charge transfer resistance was not determined, and only recorded curves are presented here. Further work will be required in order to identify more suitable test conditions or to correlate the noise with microstructural features/conditions, e.g. the amount of open pores, isolating hydrogen gas bubbles or passive/active conditions in the pores.

23) Final potentiodynamic polarization scan using the same parameters as for test 2).

3. Results

3.1. Surface appearance and porosity

The surfaces produced under otherwise constant process parameters in the three electrolytes are shown in Fig. 1. As can be seen, increasing the concentration of the electrolyte reduced the number of visible pores on the surface remarkably. In contrast, the addition of CrO_3 to the high concentration electrolyte appears to slightly increase the number of pores visible in the coating thus produced. This was also confirmed by reaction marking and counting of the open pores yielding a pore density of 136 pores/mm^2 for the standard electrolyte. For the high concentration version of the electrolyte only 24 pores/mm^2 were counted, and 30 pores/mm^2, respectively, for the CrO_3 addition. However, this variation is within the statistical error, suggesting that the addition of CrO_3 is neither beneficial nor detrimental for the pore formation. These results are displayed in Fig. 2.
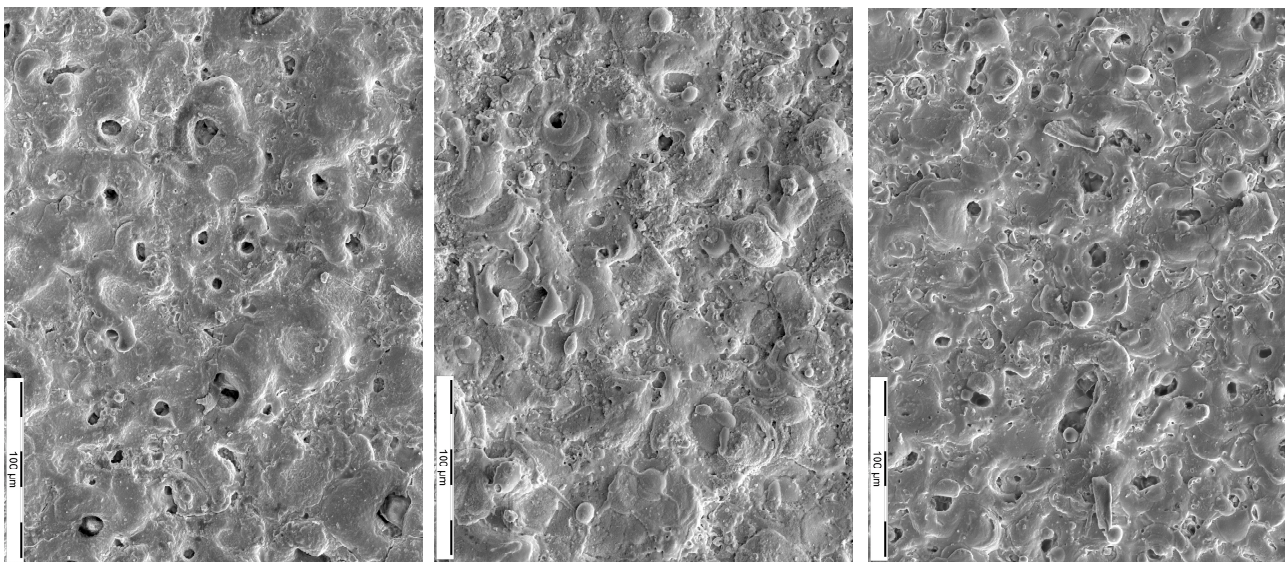
a)   b)   c)

Fig 1: Appearance of the surfaces after treatment in the various electrolytes: (a) standard, (b) high concentration, (c) high concentration + CrO3.
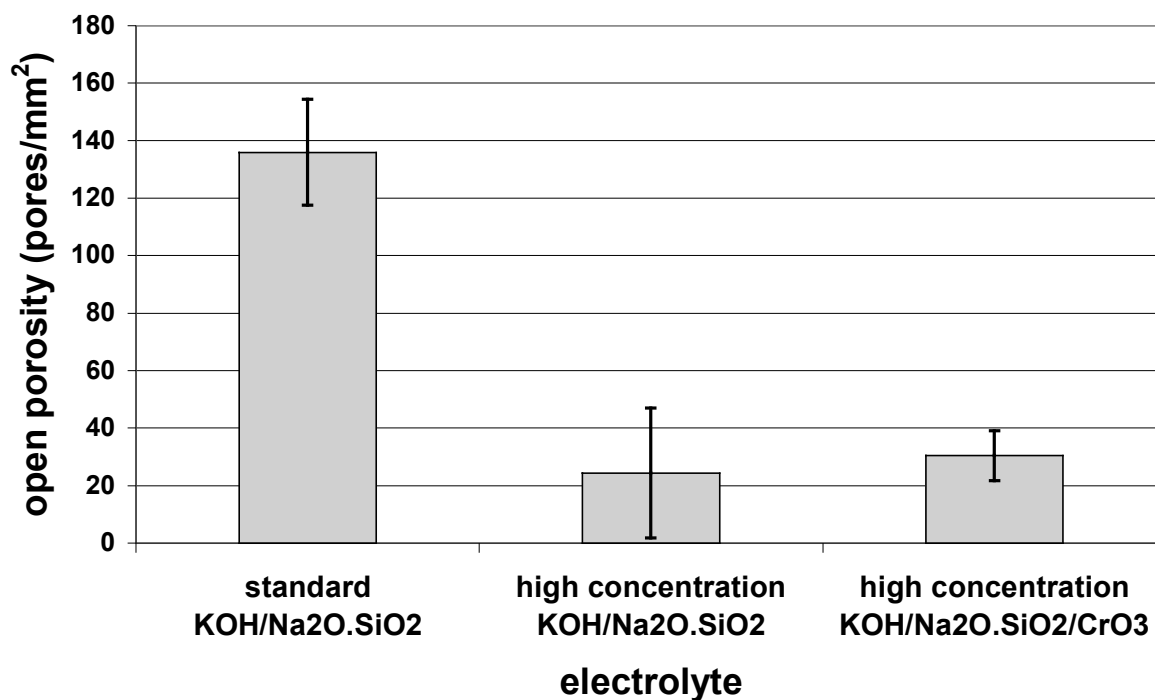
Fig 2: Number of open pores determined after reaction marking.

3.2. Elemental and phase composition

The element composition determined by EDX is displayed in Fig. 3. Not surprisingly, the amount of silicon in the layer can be increased from about 9% to about 18% if the concentration of potassium hydroxide and water glass in the electrolyte are increased. As a consequence, the amount of magnesium is reduced from about 34% to 21%. The oxygen content is slightly affected and increases from 53% to 60%, suggesting that higher oxygen containing phases formed. The addition of CrO_3 to the electrolyte reduced the effect of the higher electrolyte concentration, thus the content of silicon and oxygen was reduced to 16% and 55%, respectively, while the amount of magnesium increased again to 27%. However, not much chromium was incorporated in the layer (0.6%). Another interesting aspect is the incorporation of Al into the layer regardless of the presence of chromium or the electrolyte concentration. The amount of aluminium in the layer is higher for the low concentration electrolyte (3.5 compared to 1%). The source of the aluminium is not clear. Commercial electrolytes were used, and these can be contaminated from aluminium treatments in the same electrolyte or from aluminium impurities in the water glass.
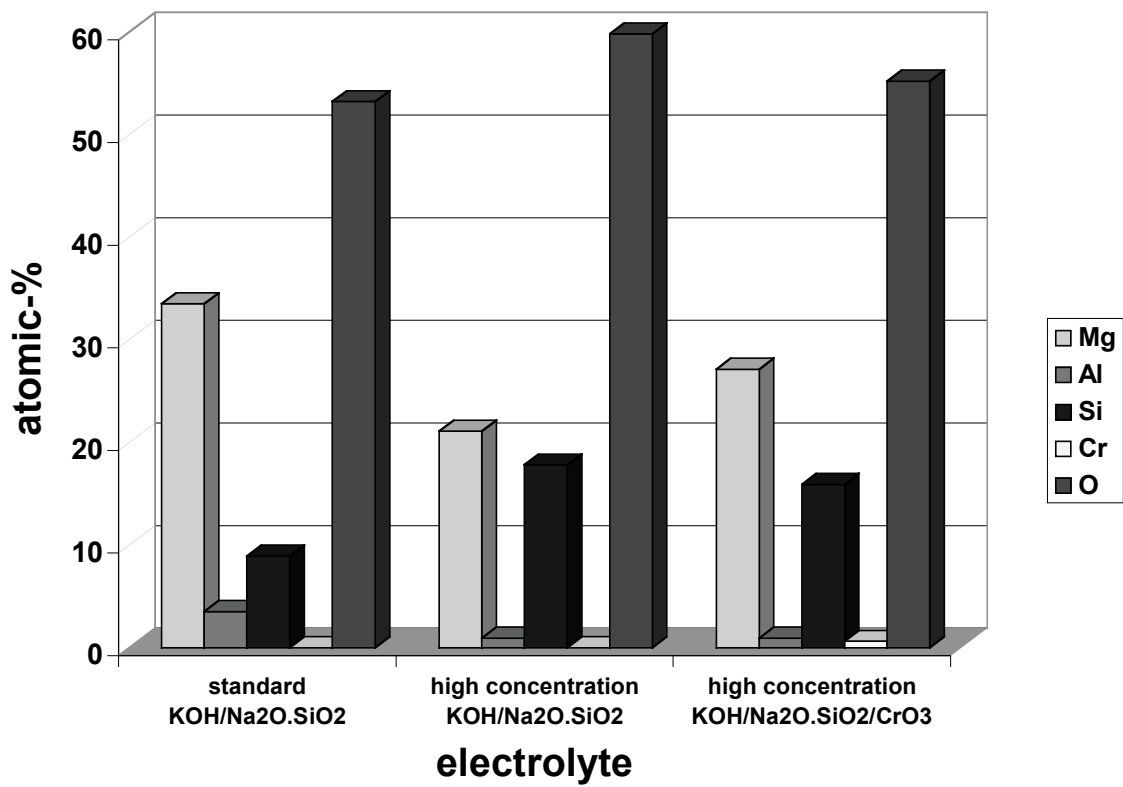
Fig 3: Elemental composition of the various layers determined by EDX analysis.

The change in the elemental composition is also visible in the phase composition determined by XRD. All layers are composed by a mixture of MgO and Mg_2SiO_4 in various amounts. Table 2 depicts the relative intensity taken for the maximum intensity peaks of Mg, MgO and Mg_2SiO_4. Whether there is elemental Mg in the layer or whether the peaks are resulting only from the substrate underneath, can not be decided. For the treatments in the high concentration electrolytes the amount of Mg_2SiO_4 (Forsterite) is increasing while the amount of MgO is reduced. This corresponds very well with the Si and O contents of the layers determined by EDX, as Forsterite (Mg_2SiO_4) contains relatively more oxygen than MgO. From the relative intensity of the peaks it can be concluded that the thickness of the coating is reduced if CrO_3 is added to the electrolyte, and that also the amount of Forsterite is reduced.

| Coating	Mg	Mg0	Mg_2SiO_4
Standard	100	56.2	6.9
High concentration	100	34.2	25.3
High concentration + CrO_3	100	24.2	13.8

Tab 2: Relative intensities determined from the maximum intensity peaks of Mg, MgO and Mg_2SiO_4 and representing the amount of the respective phase.

3.3. Corrosion

The standard potentiodynamic polarization curves measured in the beginning and the end of the

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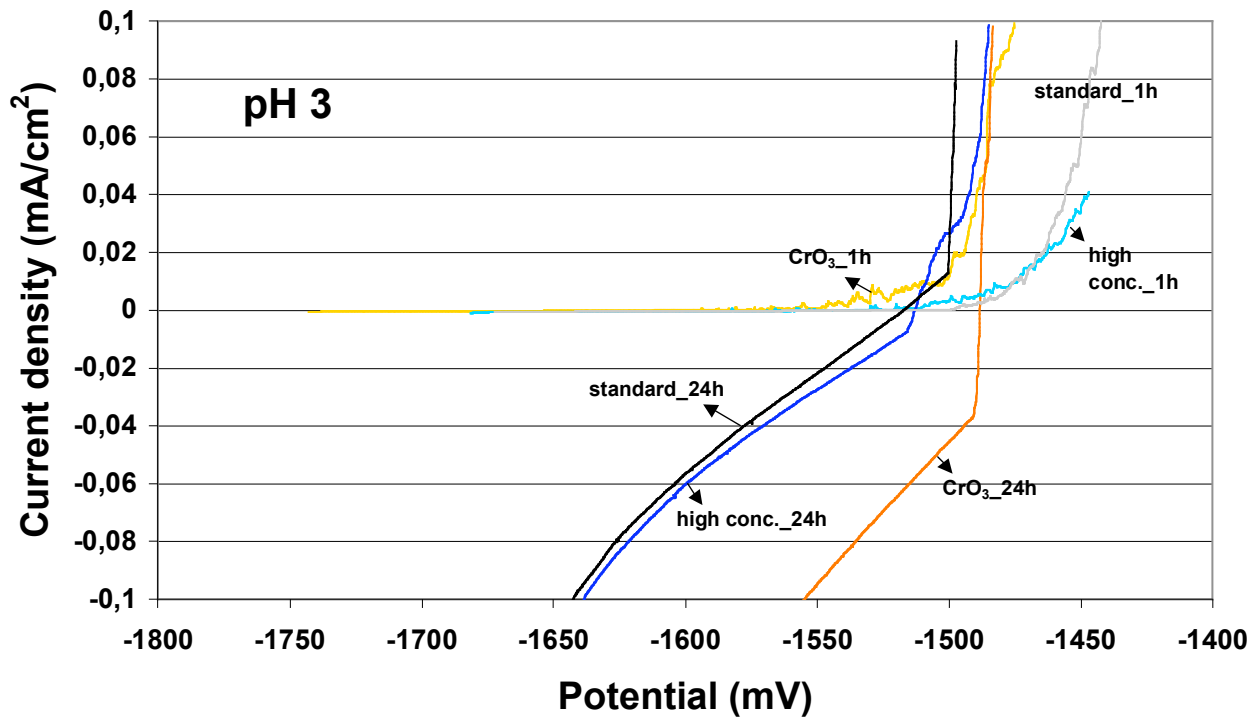
a)
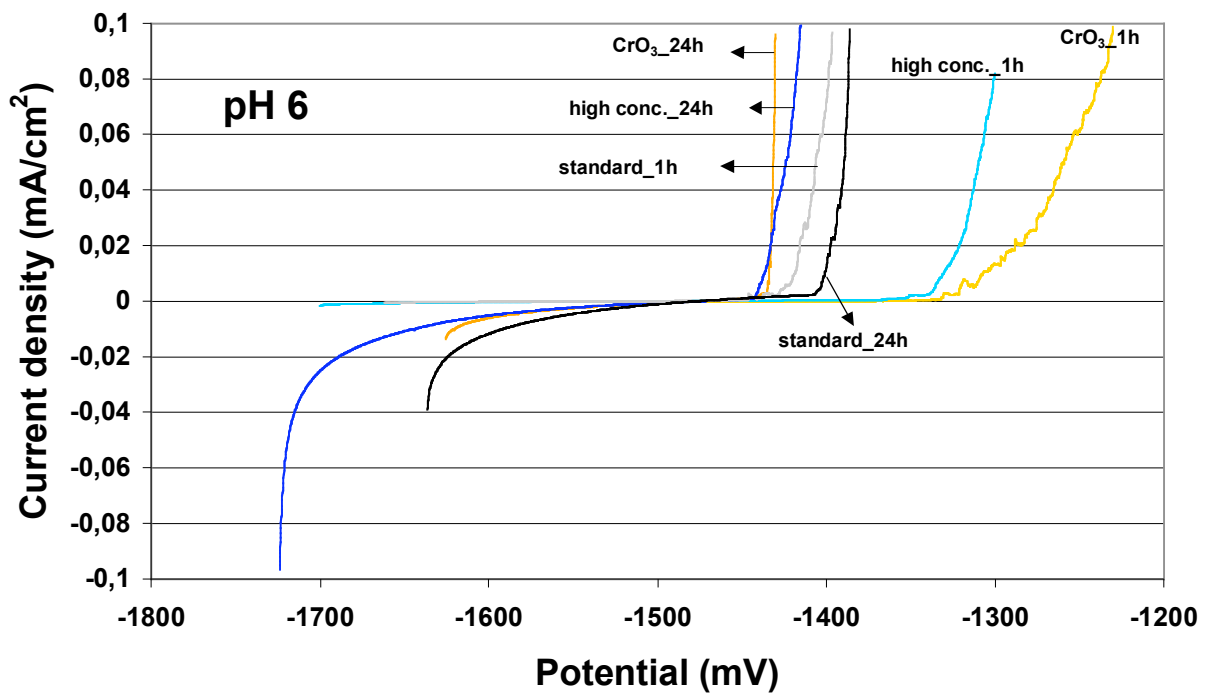
b)

Fig 4: Potentiodynamic polarisation curves for the various layers obtained after 1 hour (2nd test) and 24 hours (23rd test) determined from immersion in 5% NaCl solution at a) pH3 and b) pH6.

24 hour corrosion experiment are displayed in Fig. 4. The protective function of the coatings in the beginning was visible in low corrosion currents and larger differences between corrosion potentials and breakdown potentials, taken as the voltage at which the corrosion current significantly increased (Table 3). Note that none of the specimens showed a real passive region. In both solutions the corrosion currents were lower during the first run, and the break through potentials indicating active corrosion of the substrate were much higher (shifted towards more noble potentials) compared with the final scan, indicating a corrosion damage of all coatings (Table 3). For the long term immersion in acid solution almost no passive region was observed anymore, which is consistent with the observed large-area flaking off of the protective coating.

Coating	E_{corr}, pH3, 1h	E_{break}, pH3, 1h	E_{corr}, pH3, 24h	E_{break}, pH3, 1h	E_{corr}, pH6, 1h	E_{break}, pH6, 1h	E_{corr}, pH6, 24h	E_{break}, pH6, 24h
Standard	-1530 mV	-1514 mV	-1518 mV	-1500 mV	-1515 mV	-1447 mV	-1476 mV	-1407 mV
High concentration	-1535 mV	-1530 mV	-1516 mV	-1501 mV	-1506 mV	-1365 mV	-1475 mV	-1440 mV
High conc. + CrO_3	-1612 mV	-1602 mV	-1489 mV	-1489 mV	-1450 mV	-1365 mV	-1478 mV	-1442 mV

Tab 3: Corrosion potentials and breakdown potentials (versus Ag/AgCl reference electrode) determined from standard polarisation tests in 5% NaCl at pH3 and pH7 at the beginning and at the end of an electrochemical test sequence with a total duration of 24 hour.
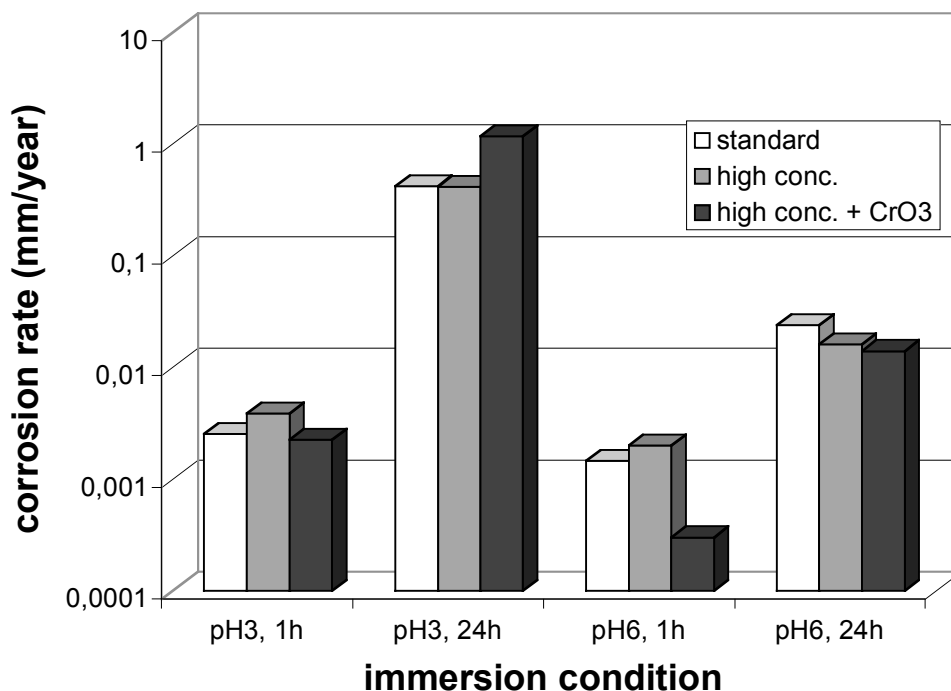

Fig 5: Corrosion rates determined from the standard polarisation tests in 5% NaCl solution at pH 3 and 6

constant during the tests (Fig. 6). Such instabilities should be expected considering the damage on the specimens. While optically none of the specimens was largely damaged in the pH6 salt solution, all specimens exhibited large surface areas with a flake off of the top layers in the pH3 solution (Fig. 7). An explanation for the instabilities may be an increase of the pH in the pores due to the corrosion of magnesium, the formation and trapping of electrically insulating hydrogen bubbles in the pores, delamination of the interface, and flake off of coating areas. Further work will be required to specify more suitable test conditions or to correlate the noise with microstructural and/or corrosion features. Because of the changing conditions during the tests, the results are not suitable for a detailed evaluation. However, the results indicate that the layer corrosion resistance is more continuously decreasing in the slightly acidic solution while it is rapidly dropping (already during the first EIS measurement) to low values in the more acidic solution, i.e. at pH3.

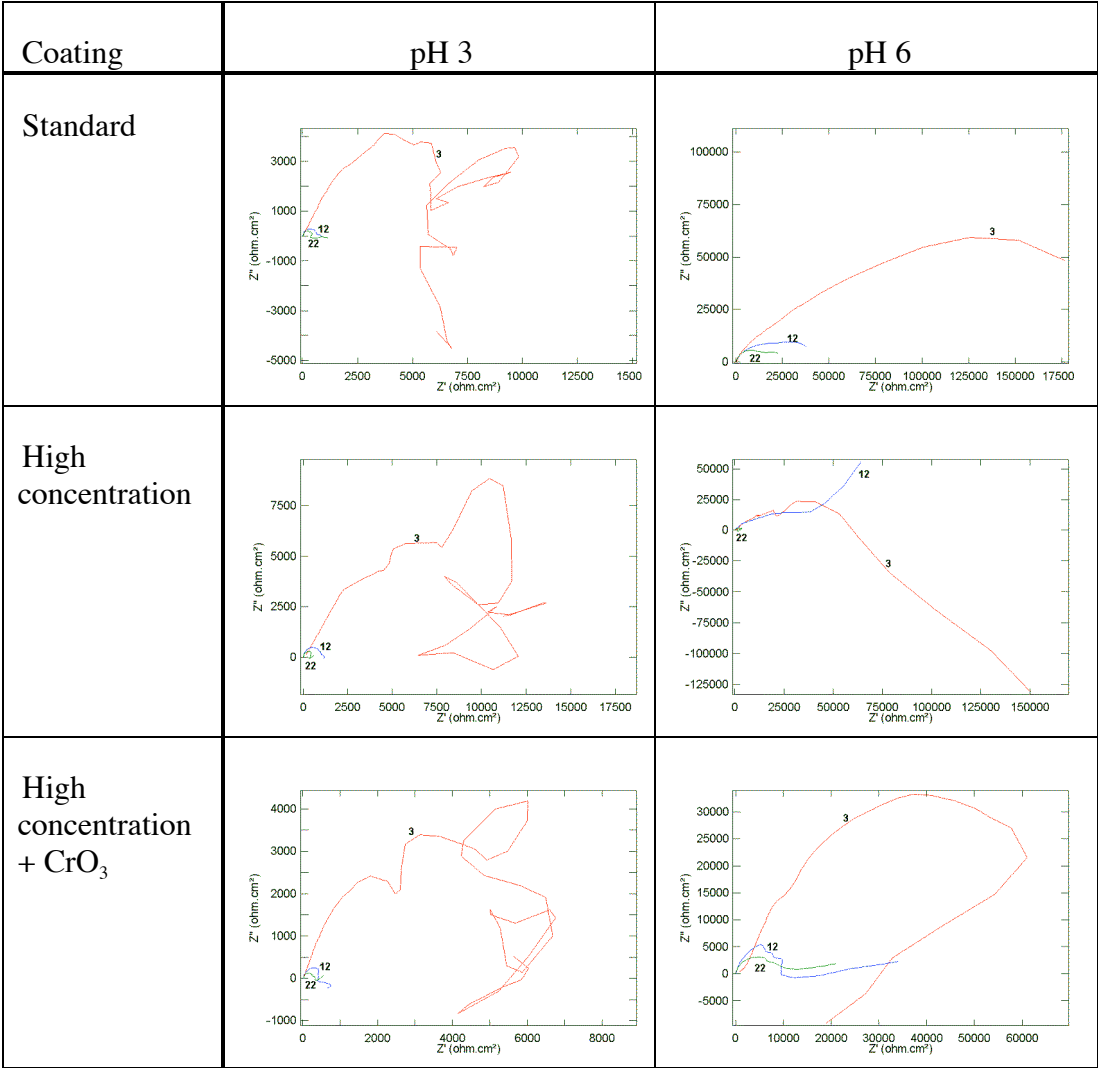| Coating	pH 3	pH 6
Standard		
High concentration		
High concentration + CrO$_3$		

Fig 6: Impedance spectra (Nyquist plots) measured for the various layers at the beginning (3), the middle (12) and the end (22) of the EIS test sequence.
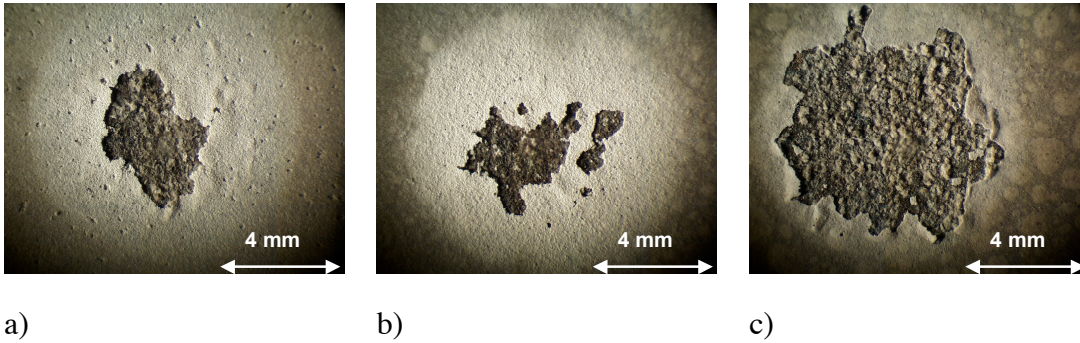
Fig 7: Surface appearance after 24 hours immersion in 5% NaCl solution at pH3 and a sequence of electrochemical corrosion tests performed during this immersion time: (a) standard, (b) high concentration, (c) high concentration + CrO₃.

4. Discussion

The easiest way to reduce the pore density for the given process conditions and for the base electrolyte used in the present study would be to increase the concentration of the electrolyte. Under otherwise identical process conditions the open pore density wais reduced by a factor of 6 if the electrolyte concentration was increased by a similar factor. Although this should have had a positive effect on the corrosion resistance of the layer such improvement was not observed under the aggressive test conditions used in this study. Passivation of the open pores by an after-treatment in boiling distilled water may offer reasonable short-term protection but is not sufficient for long-term exposure or more aggressive environments. Without sealing, the potential use of all three coatings tested here in acid surrounding would be very limited.

The use of CrO_3 which is beneficial in many coating processes for magnesium alloys was not effective under the parameters used in the present plasma electrolytic oxidation process. It did neither improve the process conditions nor did it contribute to a significantly better corrosion performance when it was incorporated into the protective oxide layer. There is some indication regarding short term improvement, but in the long term the incorporation of chromium revealed a detrimental effect on the coating adhesion to the substrate, visible in an increase of the coating delamination and flaking off. Obviously, chromium species were not released from the PEO coating surrounding open pores, and therefore no long-term corrosion inhibiting effect was observed. Hence, taking into consideration the strict regulations and limitations for the use of hexavalent chromium and its poor performance in plasma anodized coatings there is no justification for its use in PEO processes. The increase of the electrolyte concentration alone has a similar effect on the corrosion performance. Yet, the idea of incorporating inhibiting species into the layer may work with other inhibitors.

A critical aspect has been the adhesion of the layer to the substrate during testing in acid solutions, as all specimens suffered from delamination or, even worse, from flaking off of larger coating areas. The mechanism is not yet clear, but optical observations during and after the corrosion tests suggest that the delamination is caused by hydrogen gas evolution and the formation of insolvable corrosion products if the acidic environment reaches the interface. The pressure and/or volume increase in the limited space of the pores cause high stresses which will result in delamination. The influence of the pore density is not so important as long as any pores

are available as initiation sites for the delamination. Once delamination has initiated, the pore density is of no influence anymore. Compared to acidic test solutions, alkaline solutions are less aggressive and delamination caused by accumulation of corrosion products requires much longer times, so that the pore density (exposed area) controls the corrosion rate as was observed in our previous work [9]. The same work also gave some evidence of the delamination mechanism in acidic solutions.

An additional effect weakening the coating in the present work may be the dissolution of less corrosion resistant parts of the coating itself. Although there was no indication of a larger delamination on the specimens prepared in the high concentration electrolyte, the phase mixture of MgO and Mg_2SiO_4 may cause additional problems especially if the specimens are at the same time exposed to alternating thermal loads. However, the specimens prepared in the electrolyte with addition of CrO_3 suffered from the strongest flake off, indicating that the addition of CrO_3 had a negative effect on the adhesion and therefore on the overall corrosion resistance. A clear correlation between the open pore density and the degree of flaking was not evident in the present study. Unfortunately, all three coatings used in the test not only had different pore densities but also different phase compositions. While a low pore density may have a positive effect on the tendency for flaking, an increasing amount of second phase could have the opposite effect. As a consequence, the specimens produced in the high concentration electrolyte and having the lowest pore density but the largest volume fraction of a second phase in the coating, may perform similar to the specimens prepared in the standard electrolyte having a high pore density but a low amount of second phase. Further work will be necessary to better understand the mechanism.

5. Conclusions

The corrosion performance of the PEO coatings correlates generally with the open pore density, although the influence is reduced with decreasing the pH. In acidic surroundings, flaking is the dominant mechanism determining the corrosion resistance of unsealed PEO coatings based on MgO and Mg_2SiO_4.

A potential way to reduce the pore density and to improve the corrosion performance at least in alkaline to neutral environments would be to increase the concentration of the components in the electrolyte. Addition of CrO_3 is not only undesirable from an environmental point of view but is also useless for improving the corrosion performance. Although chromium species were incorporated into the layer they yielded no better inhibiting capabilities of the PEO coating.

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