Final Draft
of the original manuscript:

Influence of pH on the deterioration of plasma electrolytic oxidation coated AM50 magnesium alloy in NaCl solutions

J. Liang, P. Bala Srinivasan*, C. Blawert, W. Dietzel

Institute of Materials Research

GKSS-Forschungszentrum Geesthacht GmbH

D-21502 Geesthacht, Germany

*Corresponding Author (bala.srinivasan@gkss.de);

Phone: 00-49-4152-871997; Fax: 00-49-4152-871960

Abstract

The corrosion deterioration process of plasma electrolytic oxidation (PEO) coatings on AM50 magnesium alloy prepared from two different based electrolytes, i.e. an alkaline phosphate electrolyte and an acidic fluozirconate electrolyte, were investigated using electrochemical impedance spectroscopy (EIS) in a 0.1 M NaCl solution with pH of 3, 7 and 11, respectively. It was found that the PEO coating formed in alkaline phosphate electrolyte, which was composed mainly of MgO, suffered from rapid chemical dissolution and lost its protection capability very quickly in acidic NaCl solution (pH 3). The chemical dissolution of this PEO coating was retarded in neutral NaCl solution (pH 7) and the corrosion damage was localized in this environment. On the other hand, in the alkaline NaCl solution (pH 11), the MgO coating underwent only slight degradation. The PEO coating produced in acidic fluozirconate electrolyte, the failure was marked by the flaking-off of the large areas of coating in acidic NaCl solution (pH 3). However, in the neutral and alkaline NaCl solutions, the coating underwent only a slight degradation without any observable corrosion damage in the 50 h test. The results showed that the deterioration process of PEO coated magnesium alloy was governed mostly by the pH of NaCl solution and it was also strongly related to the microstructure and composition of the PEO coatings.

1. Introduction

Magnesium alloys are of great interest for many industrial applications, e.g. automotive, aerospace and communication, etc., due to their low density, good strength/weight ratio, high dimensional stability, good electromagnetic shielding and damping characteristics, good machining and recycling ability [1,2]. However, a critical limitation for the extensive application of magnesium alloys is their susceptibility to corrosion, especially in chloride environments [3-5]. Many attempts are being adopted for overcoming the corrosion problems. These include the effective addition of alloying elements, control of impurities,

control of microstructure through rapid solidification, modification of surfaces by suitable treatments and so on [6]. Among these techniques, surface treatment seems to be one of the most effective ways to improve the corrosion resistance of magnesium alloys. Various surface treatments, such as plating, conversion coatings, anodizing, gas-phase deposition, laser surface alloying and polymer coatings, are currently in use, amidst which the plasma electrolytic oxidation (PEO) treatment is becoming increasingly popular in the last few years [7-11]. By the PEO process a relatively thick, dense and hard oxide coating can be produced on the surface of magnesium alloys to improve their corrosion resistance remarkably [12-15].

The influence of pH and/or chloride ion concentrations on the corrosion of pure magnesium and magnesium alloys has been studied extensively for understanding of environmental factors controlling corrosion [3,16-20]. From a practical view point, it is worthwhile to investigate and understand the influence of environmental factors on the corrosion behaviour of surface treated magnesium alloys. To date, however, there is not much published information on the effect of pH and/or chloride ion concentrations on the corrosion of surface treated magnesium alloys, excepting a publication by the authors' group, which gave some insights into the corrosion behaviour of PEO coated magnesium alloy in acidic and neutral solutions [21]. In order to fully understand the corrosion mechanism of PEO coated magnesium alloy in different corrosive environments, two kinds of PEO coatings with different phase composition and microstructure were produced and their deterioration process was evaluated by electrochemical impedance spectroscopy (EIS). The corrosion behaviour and mechanisms of PEO coated magnesium alloy in chloride environments of different pH levels were assessed and discussed.

2. Experimental

Test coupons (15 mm × 15 mm × 4 mm) of AM50 magnesium alloy (mass fraction: 4.4% ~ 5.5% Al, 0.26% ~ 0.6% Mn, max 0.22% Zn, max 0.1% Si, and Mg balance) were used as the substrate for the PEO treatment. The specimens were ground with different grit emery sheets (up to 2500 grit) before the PEO treatment. The PEO processing conditions were exactly similar to those reported in our earlier work [22].

Macroscopic surface appearance of the corroded samples after corrosion tests were examined in a stereo-zoom optical microscope. Scanning electron microscope (Cambridge Stereoscan) was employed to observe the surface morphology of PEO coated samples, both before and after corrosion tests, which were sputtered with thin gold film in order to prevent surface charging effects.

Electrochemical corrosion tests were carried out using a computer controlled Gill AC potentiostat/frequency response analyser to evaluate the deterioration process of PEO coated magnesium alloy specimens in NaCl solutions. A typical three electrode cell, with a saturated Ag/AgCl (saturated with KCl) as reference

electrode, a platinum mesh counter electrode and the PEO coated specimen as the working electrode (0.5 cm^2 exposed area) were used in the tests. All electrochemical tests were conducted in 0.1 M NaCl solution with pH of 3, 7 and 11; the pH of the solutions was adjusted to the desired value with HCl and NaOH. The electrochemical impedance spectroscopy (EIS) tests were performed at open circuit potential with AC amplitude of 10 mV over the open circuit potential in the frequency range from 30,000 Hz to 0.01 Hz after immersion periods of 0.5 h, 2 h, 5 h, 10 h, 25 h and 50 h, respectively. All experiments were performed at room temperature, i.e., 21 ± 1 °C, and the NaCl solution was stirred with a magnetic stirrer during the electrochemical measurements. All electrochemical tests were conducted in triplicate in order to ensure the reproducibility of results.

3. Results

3.1 Composition and microstructure

In our previous work [22], the phase composition and microstructure of the PEO coatings prepared from the two different electrolytes have been investigated systematically. X-ray diffraction (XRD) analyses indicated that the PEO coating produced in alkaline phosphate electrolyte was mainly composed of MgO. The PEO coating that was prepared in acidic fluozirconate electrolyte consisted mostly of tetragonal ZrO$_2$ (t-ZrO$_2$) and monoclinic ZrO$_2$ (m-ZrO$_2$) phases along with MgF$_2$ and a very little of MgO. According to the main phase composition of coated specimens identified in XRD, the PEO coatings prepared from alkaline phosphate and acidic fluozirconate are addressed as "MgO coating" and "ZrO$_2$ coating", respectively, in the following discussions.

The surface and cross-section morphologies revealed that the surface of the ZrO$_2$ coating was very rough (R_a = 3.6 ± 0.6 μm) and there existed many large irregular-shaped pores and micro-cracks. The thickness of the ZrO$_2$ coating was around 40 ± 8 μm. The MgO coating was relatively smooth with a roughness value of R_a = 2.2 ± 0.2 μm and the micropores appeared to be sealed or partially-sealed internally. The major part of the MgO coating in cross-section was compact with a thickness of 28 ± 5 μm. Overall, from the point of view of the microstructural characteristics of these PEO coatings, it was concluded that the ZrO$_2$ coating has a higher pore density while the MgO coating was relatively compact.

3.2 Evaluation of corrosion deterioration by EIS

Electrochemical impedance spectroscopy (EIS) is a powerful technique to study corrosion behaviour of metals or coated metals [23-25]. In this study, EIS tests was employed to investigate the deterioration process of the PEO coated samples in 0.1 M NaCl solution at different pH, i.e. 3, 7 and 11. **Figure 1** presents the EIS behavior (Nyquist plots) of MgO and ZrO$_2$ coated magnesium alloy exposed to 0.1 M NaCl solution of pH 3. At the initial stages of the test, viz., after 0.5 h immersion, the MgO specimen exhibited larger capacitive loops, indicating that it provided an effective corrosion protection even in this aggressive acidic solution. However, the dimension of capacitive loop shrank

remarkably after 2 h of exposure, suggesting the rapid degradation of the coating. With the prolonged immersion beyond 2 h, it can be seen from the inset in Figure 1a that the dimension of capacitive loops shrank further to very low levels.   The drop in the order of magnitude of corrosion resistance after 5 h of exposure was less significant, and it can be observed that beyond 5 h of exposure most of the MgO coating disappeared and magnesium alloy substrate got exposed to the NaCl solution. On the other hand, the ZrO_2 coated specimen exhibited smaller dimension of capacitive loops in comparison with the MgO specimen at the initial 0.5 h immersion as can be seen in Figure 1b, which means that it has a lower corrosion resistance. After 2 h of exposure the resistance dropped to a lower value. The resistance dropped further after 5 h of exposure, and remained nearly the same after 10 h, as well.   In the cases of exposures of 25 h and 50 h, inductive loops were registered in the Nyquist plots (inset in Figure 1b).

In the NaCl solution of pH 7, the dimension of capacitive loop of the MgO coating was as large as those in pH 3 NaCl solution at the initial 0.5 h immersion test **(Figure 2a)**. The deterioration of the coating was evident in the test after 2 h of exposure. The corrosion resistance of the coating was more or less the same after 5 h and 10 h of exposures, and with further increase in exposure time the resistance values dropped drastically.   Inductive loops were evidenced in the 25 h and 50 h EIS tests, suggesting the possibility of a localized damage to the coating. In the case of the ZrO_2 coating, quite differently from the obvious shrinking of capacitive loops in acidic solution, the Nyquist plots underwent only a irregular dimensional variation in a small extent with increasing immersion time as shown in **Figure 2b**. No inductive loops were observed in the Nyquist plots for this coating even in the specimen tested after 50 h of immersion, suggesting the absence of any localized damage.

When the pH of NaCl solution was increased to 11, a totally different corrosion behaviour was observed for the MgO coating **(Figure 3a)**. With increasing immersion time up to 10h, there was a marginal shrinking for the dimension of capacitive loops. It was also noted that the dimension of capacitive loops even expanded after 25 h immersion. The ZrO_2 coating also exhibited relatively larger dimension of capacitive loops in NaCl solution at pH 11 compared to those in acidic and neutral solution and the Nyquist plots showed resistance values of 30 – 40 kΩ.cm² for entire immersion process up to 50 h as is seen in **Figure 3b**.

The impedance data at low frequency (for example, 0.1 Hz), can be considered as an indication of the corrosion resistance (R) of the sample, i.e. R is approximate equal to $|Z|_{f=0.1\ Hz}$ **[24,26]**. In this way, the corrosion resistance values of the samples were determined from the magnitude of the impedance data at 0.1 Hz, as a function of immersion time and are presented in **Figure 4** (with 10% experimental error). It can be seen that the resistance of the MgO coating is very high (*ca.* 250 kΩ·cm²) at initial 0.5 h of immersion in acidic NaCl solution as can be seen in **Figure 4a**. However, the corrosion resistance decreased rapidly with immersion time and it was below 1.0 kΩ·cm² after 5 h immersion, which was very close to the resistance of the bare magnesium alloy

in this environment, suggesting that there was no corrosion protection from the coating any more. Nearly the same corrosion resistance was registered for the MgO coating in neutral (pH 7) NaCl solution to that observed in acidic NaCl solution after initial 0.5 h of immersion (**Figure 4a**). Similarly, the corrosion resistances also decreased with immersion time, but the decrease rate of corrosion resistance was slower than that in pH 3 solution, suggesting a milder deterioration of the MgO coating in this neutral environment. In alkaline NaCl solution of pH 11, a significantly higher corrosion resistance (*ca.* 1,000 k$\Omega \cdot$cm^2) compared to those in acidic and neutral solutions was registered for the MgO coated specimen tested after 0.5 h of exposure. With increasing immersion time, the corrosion resistance decreased from *ca.* 1,000 k$\Omega \cdot$cm^2 at 0.5 h to *ca.* 425 k$\Omega \cdot$cm^2 at 10 h, and after 25 h, the resistance increased slightly and registered a stabilized value of *ca.* 600 k$\Omega \cdot$cm^2 in the tests performed after 25 h and 50 h of immersion.

Figure 4b shows the variation in the corrosion resistance of the ZrO$_2$ coated magnesium alloy with immersion time in NaCl solutions of different pH levels. It is clear that the corrosion resistance of ZrO$_2$ coated sample dropped rapidly in acidic NaCl solution between 0.5 h and 5 h of immersion, while the resistance was slightly higher than that of MgO coated sample after 5 h of immersion (*ca.* 2.7 k$\Omega \cdot$cm^2). After 5 h, the resistance continued to decrease with immersion time and reached a value of *ca.* 1.5 k$\Omega \cdot$cm^2 at the end of immersion tests (50 h), which is reflective of the continuous deterioration of sample. However, the resistance at 50 h was not as low as that of bare magnesium alloy sample in this condition, indicating that the coating did not fail completely. In neutral NaCl solution, the deterioration of ZrO$_2$ coated specimen was totally different from that of MgO coated sample. It can be seen from **Figure 4b** that there was no obvious decrease in the corrosion resistance with immersion time and the resistances remained in the range from 10 k$\Omega \cdot$cm^2 to 20 k$\Omega \cdot$cm^2. This suggested that this coating was relatively stable during the whole 50 h immersion process. It should also be noted that the resistance of the ZrO$_2$ coating at 0.5 h in this condition was not equal or higher than that in pH 3 solution, but was having a little lower value. It is believed that this abnormal variation is due to the complicated surface and cross-section structure of the ZrO$_2$ coating as discussed in our previous work **[22],** and the exact reason for this phenomenon could not be explained at this juncture. In alkaline NaCl solution (pH 11), the resistance values increased to some extent compared to those in acidic and neutral solutions, similar to that observed for the MgO coating, The resistances did not decrease with increasing immersion time, which varied within 30 – 40 k$\Omega \cdot$cm^2 during the 50 h immersion process. It is evident that the corrosion resistance values of the ZrO$_2$ coating after 0.5 h of immersion in all the three corrosive environments were much lower than those observed for the MgO coating, and this is attributed to the higher pore density and pore-morphology.

3.3 Corrosion morphologies
The examination of the corroded surfaces after immersion tests revealed the differences in the extent of deterioration of the MgO and ZrO$_2$ coatings in 0.1 M

NaCl solutions of different pH levels. **Figure 5** presents the macroscopic appearance of the PEO coated specimens after 50 h of EIS testing in different electrolytes. **Figure 6** shows the specific SEM micrographs of corroded area corresponding to the specimens/regions labeled in Figure 5. For comparison, the SEM surface morphologies of PEO coatings before the corrosion tests (in the as-coated condition) are also presented in Figure 6. It can be seen from Figure 5 that the MgO coating in exposed area was completely damaged, exposing the bright metal surface. The SEM micrographs in Figures 6a and b reveal that the EIS tested region has a network-like structure with plenty of mud-cracks. In the ZrO_2 coated specimen, the coating was found to have been damaged (flaked-off) in a few regions after 50 h immersion process in pH 3 solution. The SEM micrograph in Figure 6c showed that these larger damaged areas were recessed and had corrosion products in it. For other areas out of the localized corrosion damage, however, it seemed that only slight degradation had occurred on the surface (Figure 6d). It is pertinent to point out that the 25 h and 50 h EIS tested ZrO_2 coated specimens showed an inductive loop, which is suggestive of the localized damage, and the SEM micrograph discussed above corroborated the EIS results. On the other hand for the MgO coated specimen no inductive loop was observed in acidic solution and these specimens were found to undergo a uniform dissolution as affirmed by optical/SEM examinations.

In the MgO coated specimen EIS tested in neutral NaCl solution a localized corrosion was observed on the surface after 50 h immersion process. The SEM micrograph depicted in Figure 6e shows that the coating was damaged severely in a localized region and formed bumped corrosion products in it. However, the morphology in other regions of exposed area only changed a little compared to that observed before exposure to the NaCl solution as presented in Figure 6f. Even though a large part of the tested region seems to be unaffected macroscopically, the closer examination in SEM revealed that the there was a slight degradation in these regions and the damage was confined primarily on the micropores. However, in the case of ZrO_2 coated specimen, no localized corrosion damage was observed on the surface even after 50 h of immersion in NaCl solution of pH 7 (Figure 6g), which is consistent with the EIS observation. Higher magnification SEM micrograph shown in Figure 6h also revealed that the surface microstructure did not undergo any major changes compared to that the surface in the as coated condition. With the pH of NaCl solution increasing further to 11, it was found that there was no corrosion damage on the MgO coating surface after 50 h of exposure/EIS testing. SEM micrographs (Figure 6i and j) show that the surface microstructure in the exposed area had a little change compared to the original surface. For the ZrO_2 coated specimen, there was again no observable damage in the alkaline NaCl solution after 50 h of exposure/EIS testing (Figures 6k and l).

4. Discussion

From the electrochemical corrosion results and the characteristics of corroded surface, it can be found that the deterioration process of PEO coated

magnesium alloy was significantly influenced by pH value of NaCl solution and is also related strongly to the characteristics of PEO coatings.

For the MgO coated samples, the mechanism of deterioration in solutions of different pH levels can be deduced as follows: The main composition of the PEO coating, MgO, is a typical alkaline-earth oxide. In the acidic solution, MgO is easily dissolved by following reaction:

$$MgO + 2H^+ \rightarrow Mg^{2+} + H_2O \quad (1)$$

When the immersion time was short (0.5 h), the high corrosion resistance registered in EIS measurements in pH 3 NaCl solution for the MgO coating because of its relatively low defect density in the as-coated condition. With prolonged exposure, the chemical dissolution of MgO resulted in the degradation of the ceramic coating. According to Figure 1a and Figure 4a, the coating lost its protection to substrate within 5 h immersion and magnesium alloy substrate was then exposed directly to corrosive environment. In the PEO processed magnesium substrates one would expect a thin conversion film at the bottom of the pores, to be precise, at the PEO coating-magnesium substrate interface. This thin film did not offer any resistance in the acidic environment and hence the AM50 substrate comes directly in contact with the corrosive media and undergoes active dissolution. The extensive corrosion damage on the AM50 substrate on account of the above mechanism is evident in Figure 6b.

In the neutral NaCl solution, the chemical dissolution of MgO in the PEO coating was less due to the very low H^+ concentration. However, as could be seen in Figure 2a and Figure 4a, the PEO coating still suffered a quick deterioration, showing a significant drop in corrosion resistance in the EIS tests between 0.5 h and 5 h of immersion, even though the deterioration was relatively moderate than that in the acidic solution. It is speculated that the deterioration of corrosion resistance of the MgO coating at short times (to less than 5 h) may be the result of the hydrated degradation of MgO in the coating, because MgO readily reacts with water to form thermodynamically more stable Mg(OH)$_2$ in aqueous solutions [24]. The hydration processes of MgO seem to have occurred preferentially in the micropores of the coating, due to its more porous structure and higher effective surface area [24]. With the hydration of MgO, the micropores were found to be filled with the corrosion products viz., Mg(OH)$_2$. However, these hydrated products are not dense and quite porous as well, and hence would not be expected to serve as a protective barrier to corrosion attack of the underlying magnesium substrate. Therefore, the corrosion resistance of the PEO coating deteriorated quickly with the hydration of MgO in the coating. On the other hand, with prolonged immersion time (say between 5 h and 10 h), more and more Mg(OH)$_2$ was newly formed inside the micropores from hydrated MgO. Because the molar volume of Mg(OH)$_2$ is larger than that of MgO, much more newly formed Mg(OH)$_2$ inside the micropores could also result in a partial blocking of the micropores, hence retarding the further deterioration of corrosion resistance of PEO coating during

5-10 h immersion period. However, the Mg(OH)$_2$ cannot be stable in a aqueous solution with a pH lower than 10.5 [15]. Therefore, with increase in further immersion time (beyond 10 h of immersion), more amounts of fresh corrosive electrolyte permeated into the PEO coating made the formed Mg(OH)$_2$ to degrade gradually and the corrosion resistance of PEO coating then deteriorated further. Because of the fact of non-uniform structure of PEO coating in its cross-section, in the long term exposure to the electrolyte a few of the defects were converted into through-going defects in the PEO coating. Further, these defective sites expose the underneath conversion/passive film at the interface to the electrolyte. Due to prolonged exposure, the corrosive environment induced a localized damage at this interface, thus exposing the surface of the AM50 alloy substrate. This was reflected by the existence of inductive loops in Nyquist plots at 25 and 50 h immersion shown in Figure 2a. Owing to the more confined localized corrosion attack at the defective sites, the corrosion damage in the rest of the exposed area was retarded. In this way, after 50 h immersion process, a severe localized damage eventually appeared on the sample surface (Figure 6e) and the other adjoining regions underwent only a slight degradation (Figure 6f).

When the MgO PEO coated specimen was immersed into the alkaline NaCl solution of pH 11, the corrosion deterioration was only marginal between 0.5 h and 10 h of immersion, as could be seen from the EIS plots in Figure 3a. It is believed that this was resulted mainly from the unavoidable hydration of MgO in the coating. The longer immersion process (beyond 25 h of immersion), however, did not cause any further deterioration. Instead, higher corrosion resistance values were observed. The possible reason for this trend is that much more newly formed Mg(OH)$_2$ from hydrated MgO inside the micropores served as protective barrier to chloride, because Mg(OH)$_2$ is stable in aqueous solution with pH higher than 10.5. Further, the conversion film at the interface was also expected to be stable and not affected at this pH levels. The higher magnification micrographs of the corroded surface after 50 h of immersion/EIS testing showed that the micropores were covered with plenty of nano-size filament-like particles (Figures 7a and b), which was referred to as the formed Mg(OH)$_2$, and this confirmed aforementioned explanation.

In the case of ZrO$_2$ coated specimen, the existing larger density of pores and defects on the cross-section of coating, facilitated the penetration of corrosive solution to the PEO coating-substrate interface as soon as the specimen was exposed to the NaCl solution. The excessively larger pore volume was responsible for the lower corrosion resistance values observed for the ZrO$_2$ coated specimens than those of the MgO coated specimens at the initial immersion (0.5 h) in all the three corrosive environments. However, the deterioration behaviour of the ZrO$_2$ coated specimens were different with prolonged exposure in these three different environments.

In the highly acidic solution of pH 3, unlike the MgO coated specimen which suffered a severe chemical dissolution in exposed area, the ZrO$_2$ coating flaked-off in a few regions as can be seen in Figure 5. It should be pointed out

that the morphology of these flaked-off regions were different from the localized corrosion damaged regions on the MgO coating in pH 7 NaCl solution. The conversion coatings based on rare earth salt solutions is well known, and the thin films formed are expected to provide good corrosion resistance to magnesium alloys. However, the zirconate based conversion film at the interface was not stable in this acidic electrolyte, and was found to have been damaged at localized regions. Thus, the magnesium substrate underneath the coating was exposed to the electrolyte. Blawert et al. [21] suggested that the flake-off of larger coating areas in acidic solutions was caused possibly by hydrogen gas evolution and the formation of corrosion products after the acidic solution reaches the interface between the coating and the magnesium alloy substrate, because the quick increase of pressure and/or volume in the limited space of the pores caused high stresses. It was also believed that the higher pore density of the coating and higher amount of second phase may have a strong influence on the tendency for flaking. As a consequence, the ZrO_2 coating, which had a higher pore density and higher amounts of second phase, was found to be vulnerable to this form of damage. The inductive loops observed in the EIS tests performed after 25 h and 50 h exposure (Figure 1b) corroborate the macro/microstructural observations.

In the NaCl solution of pH 7, there was no pronounced corrosion damage on the surface of the ZrO_2 coated specimen (Figure 5) after 50 h of immersion/EIS testing and at the same time, the corrosion resistance kept nearly the same throughout the test period as can be seen from Figure 4b. Furthermore, higher magnification SEM micrograph (Figure 6h) revealed that the coating surface did not undergo any discernible corrosion degradation. It is thus evident in this case that the conversion film at the interface was very stable and could resist the corrosion damage. These results indicated that the ZrO_2 coating could survive much longer time (more than 50 h of immersion) than the MgO coating in neutral NaCl solution without any signs of degradation. The reason that there had been no pronounced corrosion degradation for the ZrO_2 coating in this neutral chloride solution is attributed to the fact that the ZrO_2 coating was obtained by PEO processing in an acidic electrolyte of pH 4.5, and thus the PEO coating and the conversion film at the bottom on the pores formed at this pH level could easily remain stable at higher pH values. Further, the phase compositions viz., ZrO_2 and MgF_2 are reported to have a higher chemical stability in neutral environments [22]. As a result, the ZrO_2 coating kept its integrity very well and the corrosion resistance remained nearly the same during the entire test immersion/EIS test duration.

In alkaline NaCl solution of pH 11, the ZrO_2 coated specimen exhibited a higher corrosion resistance and a more stable behaviour than those in the acidic and neutral solutions (Figure 4b). No obvious damage and coating degradation were observed even after the 50 h immersion/EIS immersion test (Figure 5 and Figures 6k,l). However, when the tested surface was examined at a much higher magnification, it was found to be covered with plenty of imperceptible particles (Figures 8a, b).   These were not observed on the corroded surface of specimens immersed/EIS tested in NaCl solutions of pH 3 and 7. Obviously,

these particles are also different from those filament-like particles on the MgO coating surface at pH 11 in shape and size. The formation of corrosion products due to the reaction of magnesium substrate underneath the PEO coating, and the consequent transfer of electrolyte-corrosion products has led to the deposition of these fine particles on the surface. One would expect the formation of similar corrosion products in neutral environment, too. However, the formation and distribution fine-corrosion products were not noticed in the earlier case, as they would have possibly been dissolved in neutral electrolyte.

5. Conclusions

1. In acidic NaCl solution (pH 3), both the MgO and ZrO_2 coatings could not provide sufficient corrosion protection to magnesium alloy substrate in longer exposures.

2. The degradation mechanisms of MgO and ZrO_2 coatings in acidic solutions were different. Whilst the MgO coating suffered from severe uniform corrosion damage owing to the rapid dissolution of the unstable MgO phase, the other coating experienced a highly localized damage as a result of flaking-off of the ZrO_2 coating.

3. In the neutral chloride environment, the corrosion resistance of the MgO coating deteriorated with prolonged immersion time and the failure after 50 h was demonstrated by the localized corrosion damage. The ZrO_2 coating, however, could survive much longer time in NaCl solution of pH 7 and no corrosion damage of PEO coating was observed. The corrosion resistance of the coating remained nearly the same throughout the 50 h immersion/EIS tests, which is attributed to the stable phase composition of the coating.

4. In alkaline chloride solution of pH 11, the MgO coating provided a much superior corrosion protection to magnesium alloy substrate. Similarly, a more stable corrosion resistance of the ZrO_2 coating than that in neutral solution was observed in alkaline NaCl solution.

References

1.   B.L. Mordike, T. Ebert, Maqster. Sci. Eng. A 302 (2001) 37.

2.   Y. Kojima, Mater. Sci. Forum. 350-351 (2000) 3.

3.   G. Song, A. Atrens, D. St. John, X. Wu, J. Nairn, Corros. Sci. 39 (1997) 1981.

4. N. Birbilis, M.A. Easton, A.D. Sudholz, S.M. Zhu, M.A. Gibson, Corros. Sci. 51 (2009) 283.

5. G. Song, A. Atrens, Adv. Eng. Mater. 9(2007) 117.

6. G. Song, Corrosion and Protection of Magnesium Alloys, Chemical Industry Press, Beijing, 2006. pp. 237-254 (in Chinese).

7. J.E. Gray, B. Luan, J. Alloys Compd. 336 (2002) 88.

8. A.L. Yerokhin, X. Nie, A. Leyland, A. Matthews, S. J. Dowey, Surf. Coat. Technol. 122 (1999) 73.

9. C. Blawert, W. Dietzel, E. Ghali, G. Song, Adv. Eng. Mater. 8 (2006) 511.

10. P. Gupta, G. Tenhundfeld, E.O. Daigle, D. Ryabkov, Surf. Coat. Technol. 201 (2007) 8746.

11. X. Zhong, Q. Li, J. Hu, Y. Lu, Corros. Sci. 50 (2009) 2304.

12. R.F. Zhang, S.F. Zhang, Corros. Sci. doi:10.1016/j.corsci. 2009.08.009.

13. C. Blawert, V. Heitmann, W. Dietzel, H.M. Nykyforchyn, M.D. Klapkiv, Surf. Coat. Technol. 200 (2005) 68.

14. J. Liang, L. Hu, J. Hao, Appl. Surf. Sci. 253 (2007) 4490.

15. R. Arrabal, E. Matykina, F. Viejo, P. Skeldon, G.E. Thompson, Corros. Sci. 50 (2008) 1744.

16. G. Song, A. Atrens, D.H. StJohn, J. Nairn, Y. Lang, Corros. Sci. 39 (1997) 855.

17. G. Song, A. Atrens, X. Wu, Z. Bo, B. Zhang, Corros. Sci. 40 (1998) 1769.

18. R. Ambat, N.N. Aung, W. Zhou, J. Appl. Electrochem. 30 (2000) 865.

19. H. Altun, S. Sen, Mater. Design 25 (2004) 637.

20. M. Zhao, M. Liu , G. Song, A. Atrens, Corros. Sci. 50 (2008) 3168.

21. C. Blawert, V. Heitmann, W. Dietzel, H.M. Nykyforchyn, M.D. Klapkiv, Surf. Coat. Technol. 201 (2006) 8709.

22. J. Liang, P. Bala Srinivasan, C. Blawert, W. Dietzel, Corros. Sci. 51 (2009) 2483.

23. C.N. Cao, J.Q. Zhang, An Introduction to Electrochemical Impedance Spectroscopy, Science Press, Beijing, 2002, p. 154-194 (in Chinese)

24. S.J. Xia, R. Yue, R.G. Rateick, Jr., V.I. Birss, J. Electrochem. Soc. 151 (3) (2004) B179.

25. Y.C. Xin, J. Jiang, K.F. Huo, G.Y. Tang, X.B. Tian, P.K. Chu, J. Biomed. Mater. Res. 89A, (2009) 717.

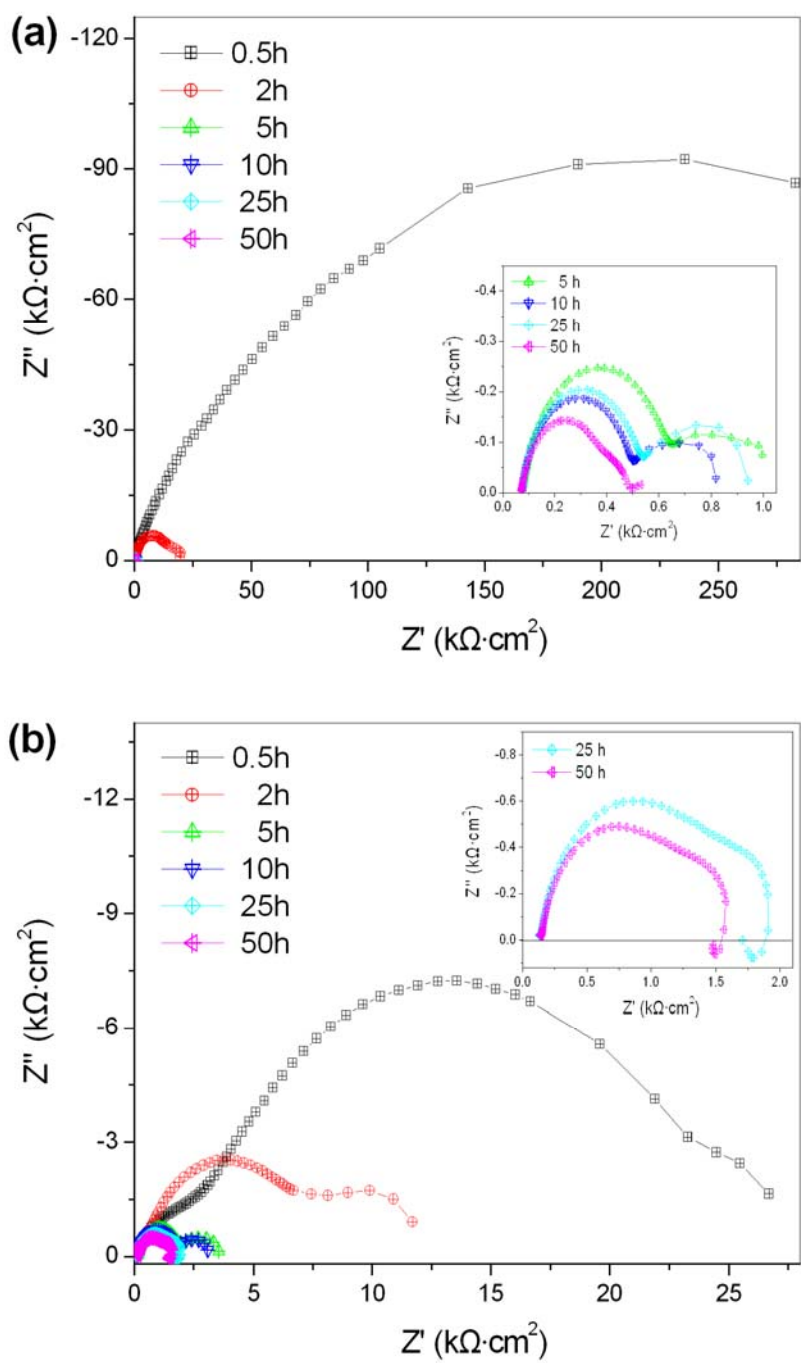26. H. Yasuda, Q.S. Yu, M. Chen, Prog. Org. Coat. 41 (2001) 273.

Figure 1 Electrochemical impedance behaviour (Nyquist plots) of (a) MgO & (b) ZrO$_2$ coated AM50 magnesium alloy in 0.1 M NaCl solution of pH 3 (after different durations of exposure).
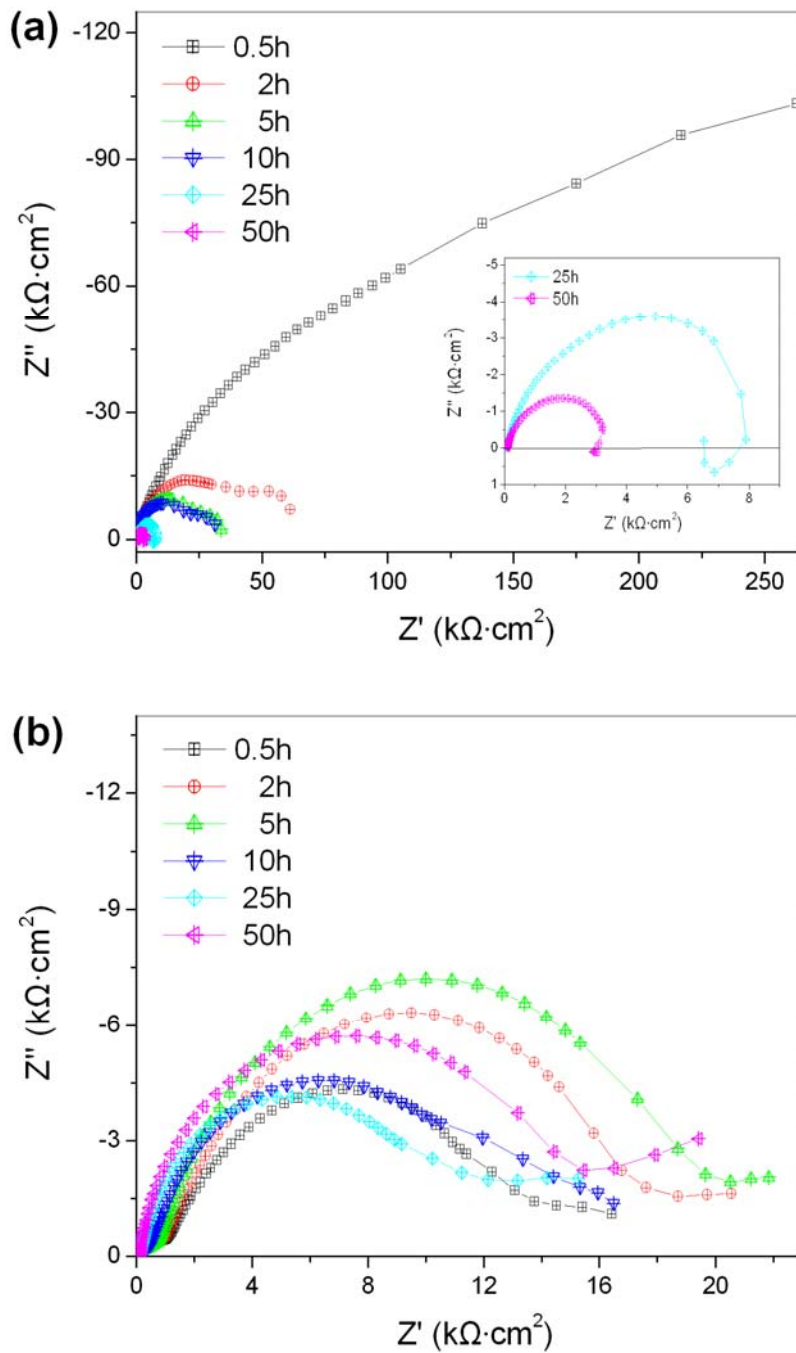
Figure 2 Electrochemical impedance behaviour (Nyquist plots) of (a) MgO & (b) ZrO$_2$ coated AM50 magnesium alloy in 0.1 M NaCl solution of pH 7 (after different durations of exposure).
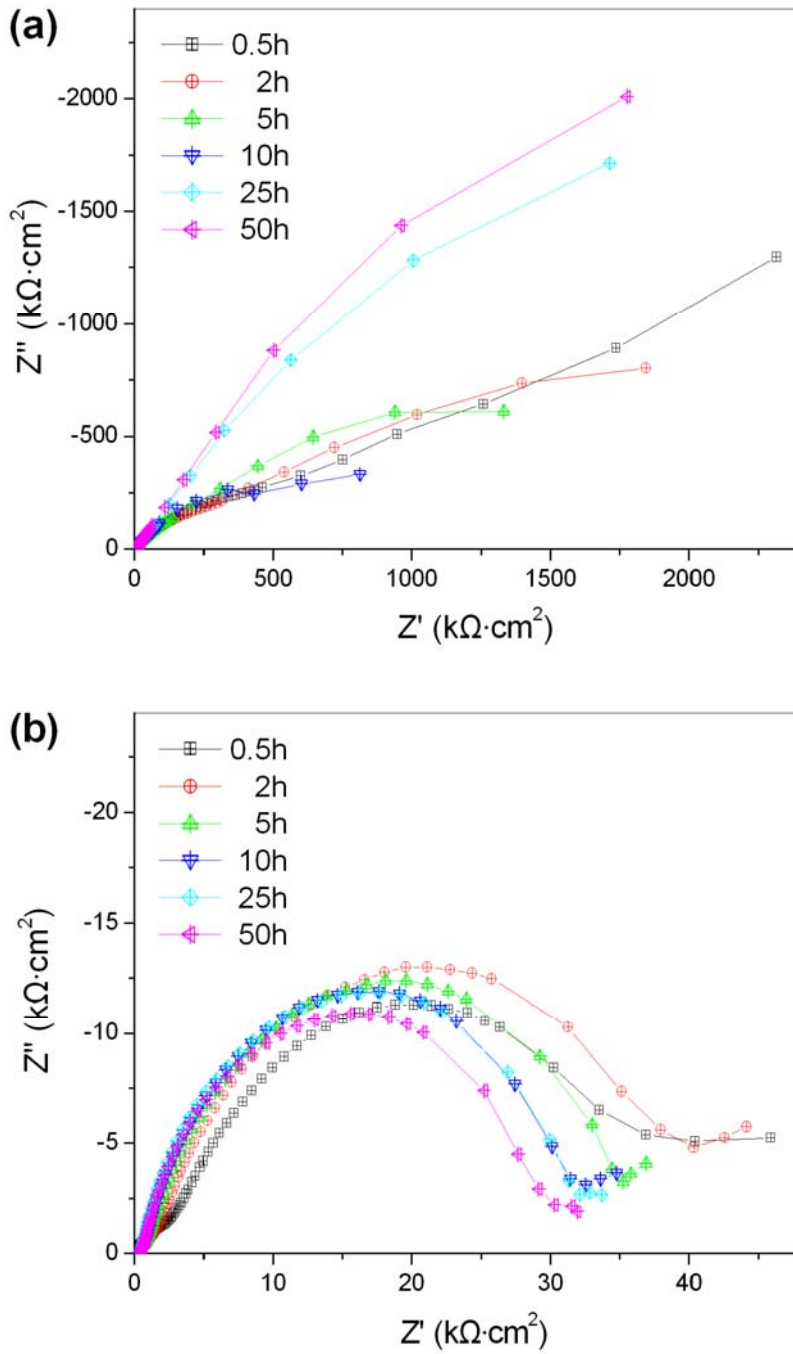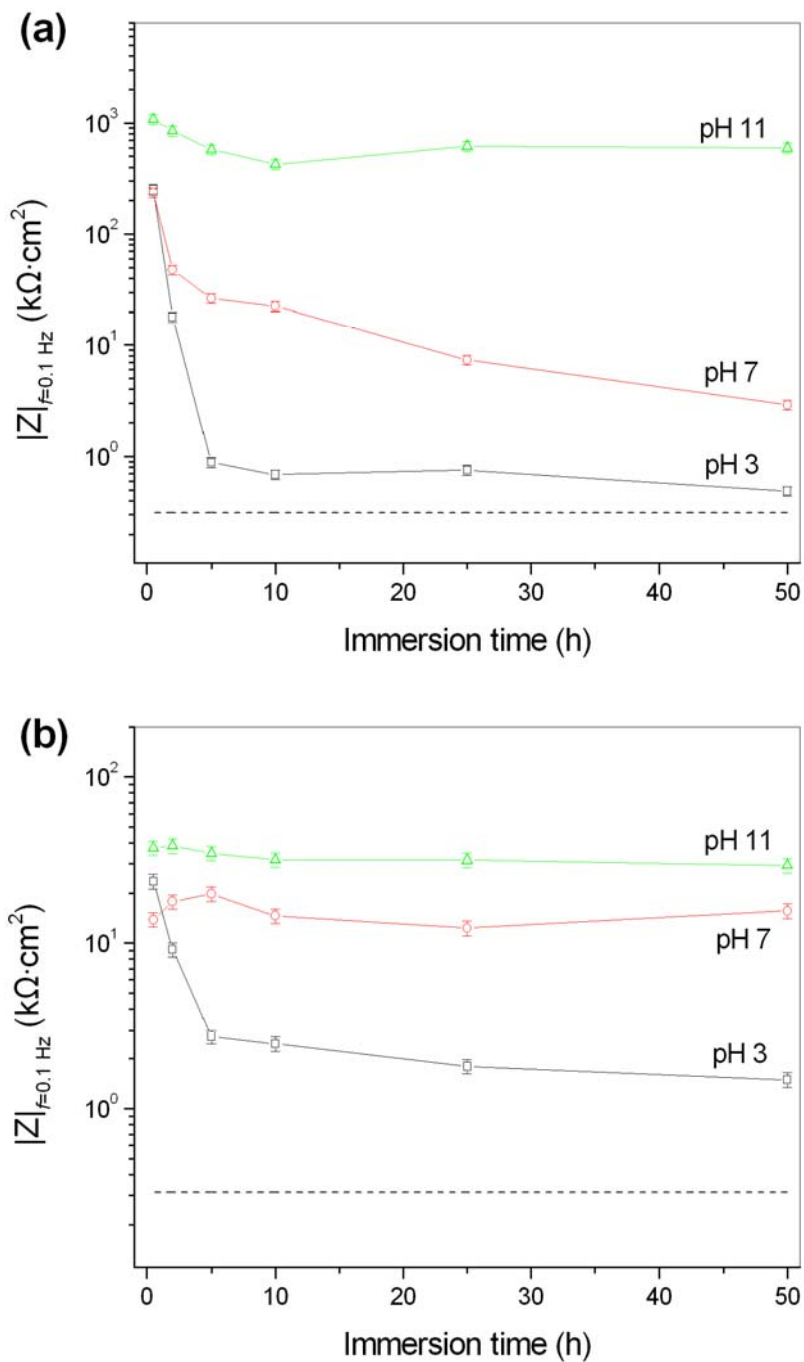
Figure 3 Electrochemical impedance behaviour (Nyquist plots) of (a) MgO & (b) ZrO$_2$ coated AM50 magnesium alloy in 0.1 M NaCl solution of pH 11 (after different durations of exposure).

Figure 4 Corrosion resistance as a function of immersion time of (a) MgO & (b) ZrO$_2$ coated AM50 magnesium alloy in 0.1 M NaCl solution of different pH levels. Dashed lines in the figures show the impedance data of uncoated magnesium alloy in 0.1 M NaCl solution at pH 3 after 0.5 h exposure.
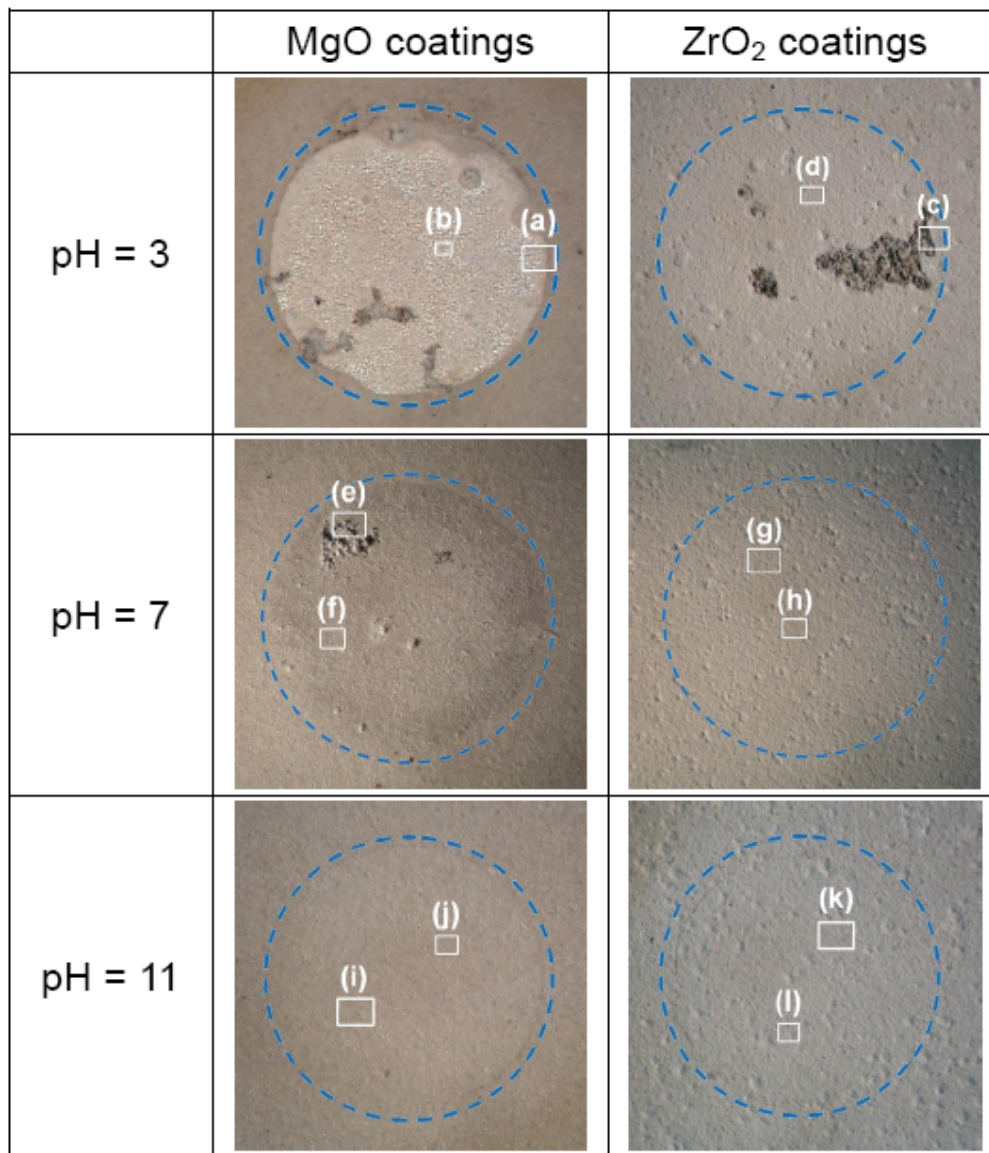
Figure 5 Macroscopic morphologies of corroded surfaces after 50h exposure/EIS testing in 0.1 M NaCl solutions of different pH levels. Dashed circles in the figures show the exposed area (0.5 cm^2) during the EIS test. Pane and letter labels correspond to the SEM micrographs in Figure 6.

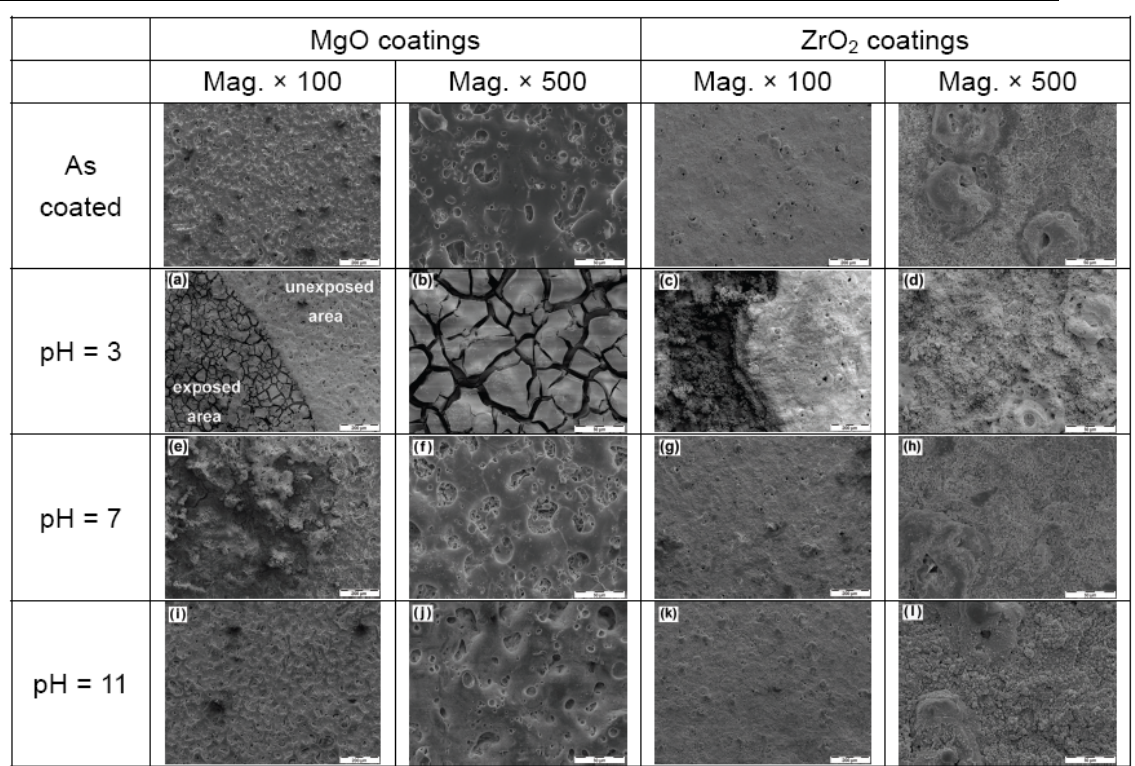|	MgO coatings		ZrO₂ coatings	
	Mag. × 100	Mag. × 500	Mag. × 100	Mag. × 500
As coated				
pH = 3	(a) unexposed area / exposed area	(b)	(c)	(d)
pH = 7	(e)	(f)	(g)	(h)
pH = 11	(i)	(j)	(k)	(l)

Figure 6   SEM micrographs of corroded surfaces after 50h immersion/EIS testing in 0.1 M NaCl solutions of different pH levels.
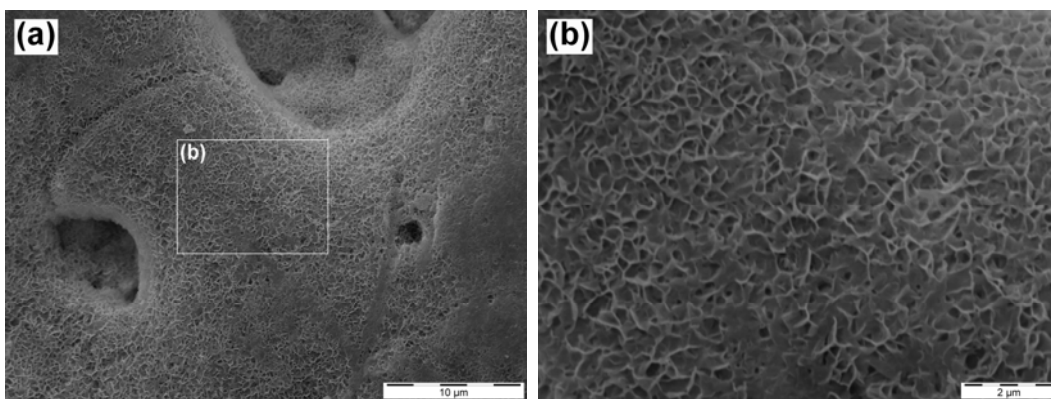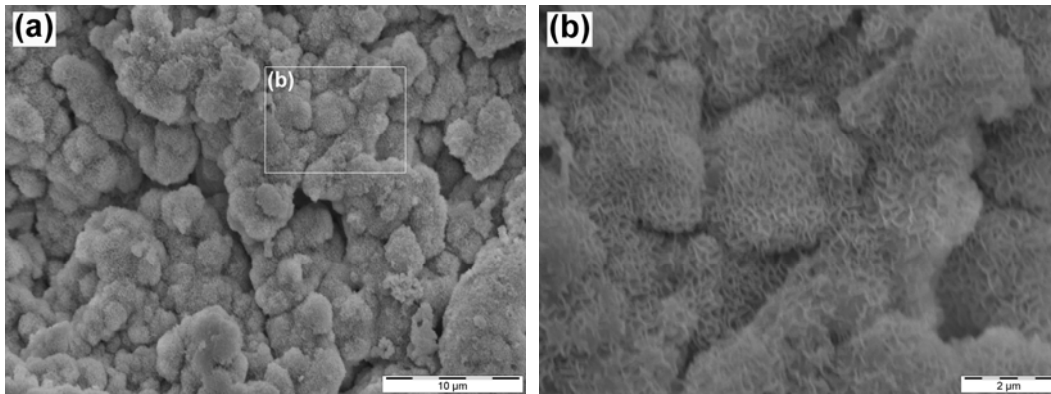
Figure 7   Higher magnification SEM micrographs of corroded surface of MgO coated AM50 magnesium alloy after 50h of exposure/EIS testing in 0.1M NaCl solution of pH 11:   (a) × 3,000; (b) × 10,000 of framed region in (a).

Figure 8   Higher magnification SEM micrographs of corroded surface of ZrO_2 coated AM50 magnesium alloy after 50h of exposure/EIS testing in 0.1M NaCl solution of pH 11: (a) × 3,000; (b) × 10,000 of framed region in (a).