

Deposition, Characterization and Electrochemical Properties of Permanganate-Based Coating Treatments Over ZE41 Mg-Zn-Rare Earth Alloy

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Rare-earth ZE41 alloy possesses unique mechanical properties. However, the sharp potential difference between the rare-earth phases (cathode) inside the Mg matrix (anode) results in building up micro-electrochemical cells and enhancing galvanic corrosion. In chloride solution, the galvanic corrosion propagates and enhances intergranular corrosion around the rare-earth phases. At the end, the rare-earth phase can be debonding from the matrix leaving holes. The optimum conditions for obtaining protective Mn-coatings of improved corrosion resistance for ZE41 alloy were determined. A simple one step surface treatment in 10 g/l Mn coating for short time was found promising to improve the localized corrosion resistance.

Keywords: Rare earth elements; Magnesium; Oxide coatings; Intergranular corrosion; Pitting corrosion; EIS.

1. INTRODUCTION

Weight reduction of automobiles is one of the most effective ways of improving fuel consumption, since the resistance of a vehicle to rolling, climbing and acceleration is directly dependent on its mass. Weight reduction in aircraft is similarly appropriate. Consequently, there is increasing research and industrial interest in the automotive and aerospace industries in replacing traditional, heavy materials with light weight materials such as magnesium- and aluminum-based alloys, and multi-material solutions, with the aim of reducing fuel consumption and CO₂ emissions. Magnesium alloys, with densities of only about one-quarter that of steel and two-thirds that of aluminum are, therefore, expected to find increasing application.

Kulekci [1], reviewed and evaluated the applications of magnesium in the automotive industry and concluded that reasonable prices and improved properties of Mg alloys will lead to massive use of

magnesium. Compared to the heavy materials currently in use, using Mg alloys results in a 22% to 70% weight reduction. In addition, the use of magnesium in automotive components is increasing as knowledge of forming processes of Mg alloys increases.

Magnesium alloys have a variety of excellent properties, including a high strength-to-weight ratio, low density, dimensional stability and castability. However, the high corrosion susceptibility of magnesium alloys, particularly galvanic corrosion, is a current challenge to overcome to enable their wider application in industry. Additionally, cost is an issue, which may be alleviated by wider use of recycled materials.

A series of magnesium alloys containing a minor percentage (0.8-1.7%) of rare-earth elements such as ZE41 has been designed by Magnesium Elektron. ZE41 is a magnesium casting alloy of medium strength which is ideal for high integrity casting operating at ambient temperatures. Moreover, as described by the manufacturer, the alloy is both pressure-tight and weldable [2].

The promising mechanical properties of this alloy make it of interest to aerospace, automotive and military materials designers. However, it has been reported that the corrosion resistance of such material is relatively low and amounted to be 4-6 mg/cm²/day (320-489 mpy) as measured by salt spray test according to ASTM B117 [2].

Chromates conversion coatings have proven to provide excellent corrosion protection to most ferrous and non-ferrous alloys due to formation of a tri/hexa-valent chromate layer of a self-healing functionality [3-14]. However, chromates have been detrimental due to their high toxicity as environmental waste and carcinogenic effects. The pressure imposed to fulfill the environmental and health regulations has been a significant driving force promoting the development of chromate free alternatives.

Many attempts have been made to improve the corrosion resistance of magnesium alloys, with different coatings and surface treatments being applied to enhance their surface resistance. Different schemes of conversion coatings based on eco-friendly salts such as molybdate, cerate, permanganate, phosphate, stannate,...etc, have been proposed as alternatives to the process involving toxic hexavalent chromate.

Ardelean, et al. [15, 16], investigated the corrosion protection of AZ91 and AM50 magnesium alloys by cerium, zirconium and niobium-based conversion coatings in Na₂SO₄ electrolyte. Electrochemical measurements showed that Mg alloys treated during 24 h in the Ce-Zr-Nb conversion bath exhibit: (i) increased corrosion potential, (ii) decreased corrosion and anodic dissolution current densities, and (iii) increased polarization and charge transfer resistances. The accelerated corrosion tests revealed excellent atmospheric corrosion resistance for all Ce-Zr-Nb-treated samples, with or without an additional layer of epoxy-polyamide resin lacquer or paint. The authors claimed that the proposed coating can replace chromates and provide improved corrosion resistance, and excellent paint adhesion for magnesium alloys.

In another study, Ardelean et al [17], successfully designed a new Nb + Zr-based anodized coating for the corrosion protection of AZ91 magnesium alloy in Na₂SO₄ electrolyte. XPS analysis indicated that the coating mainly consisted of (i) magnesium metaborate and metaphosphate, (ii) MgF₂ and ZrF₄, and (iii) Nb₂O₅, ZrO₂ and MgO. A higher concentration of fluorine at both interfaces and an

enrichment in Zr compared to Nb were revealed by SEM and EDS analyses. Thus, Zr-based compounds and MgF_2 play a key role in the anti-corrosion ability of the coating.

Chong and Shih [18], developed permanganate–phosphate coatings for AZ magnesium alloys. XRD results revealed formation of amorphous structures to cover the surface. The electrochemical polarization demonstrated that the presented conversion treatment for the series of AZ alloys had an equivalent corrosion protection potential as the JIS H 8651 MX-1 (similar to Dow No. 1) chrome-based method.

Other researchers have studied the non-chromate treatments that use acids and potassium permanganate. Takaya [19] proposed a permanganate-based bath, which provided very good corrosion resistance to AZ91D. Umehara et al. [20] also adopted permanganate, incorporated with HNO_3 or HF, as the constituents for the conversion treatment. Their study showed the corrosion resistance of the treated AZ91D to be equivalent to that of the Cr^{6+} process.

Hwang et al [21], studied the plasma electrolytic oxidation (PEO) process in AZ91 Mg alloy using a solution containing $\text{KOH} + \text{KF} + \text{Na}_2\text{SiO}_3$ both with and without KMnO_4 . It was found that the addition of KMnO_4 to the electrolyte influences coating thickness, surface morphology and the microstructure of oxide layers. Oxide layers formed by the electrolyte containing KMnO_4 consist of MgO , MgF_2 , Mg_2SiO_4 and Mn_2O_3 . The corrosion resistance of the sample processed in bath containing KMnO_4 was superior to that of the sample processed in the bath without KMnO_4 . They suggested that enhancement of the corrosion resistance of AZ91 Mg alloy depends strongly on the presence of manganese oxide in the oxide layer.

In another study, Hwang et al [22], investigated microstructure, corrosion resistance characteristics and nanohardness of the oxide layer on AZ91 Mg alloy by applying different voltage with KMnO_4 contained solution. There are lots of closed pores that are filled with another oxide compound compared with the typical surface morphology with pore coated until 350 V of coating voltage. The thickness of oxide layer increases with increasing coating voltage. The oxide layer formed on AZ91 Mg alloy in electrolyte with KMnO_4 consists of MgO and Mn_2O_3 . Corrosion potential of the oxide layer on AZ91 Mg alloy obtained at different PEO reaction stages increases with increasing coating voltage. The corrosion resistance of AZ91 Mg alloy depends on the existence of the manganese oxide in the oxide layer. The inner barrier layer composed of the MgO and Mn_2O_3 may serve as diffusion barrier to enhance the corrosion resistance and may partially explain the excellent anti-corrosion performance in corrosion test. Nanohardness values increase with increasing coating voltage. The increase in the nanohardness was attributed to the effect of manganese oxide in the oxide layer on AZ91 Mg alloy coated from electrolyte containing KMnO_4 .

However, most of the existing methods are frequently unable to produce the surface properties desired for many industrial applications, where magnesium alloys would otherwise be highly competitive. The main challenges with the existing coating methods are the cost, or they are based on multi-step coatings, with long treatment times, and involve relatively complicated procedures for formation of complex coatings with more than one oxide of elements such Si, Ce, Zr, Nb etc. Therefore, provision of eco-friendly, cost-effective, industrially-applicable coating technologies, with ready application to magnesium alloys in the transportation sector, are at the heart of this work.

Over the past two decades, Hamdy and his workgroup have successfully designed several chrome-free protective coatings that have proven to provide superior corrosion resistance and, in some cases, self-healing functionality for different magnesium alloys using stannate, vanadate, cerate, zirconate [23-38].

A new treatment focuses on a permanganate conversion coating layer has been proposed in this study. This paper reports an attempt for utilizing such coating to improve the corrosion resistance of the ZE41 magnesium alloy in chloride containing media. Permanganate salts have many advantages over most of the other salts used before in chrome-free coatings manufacturing. Permanganate salts are quite cheap compared with cerium, vanadium, zirconium, and stannate salts. Moreover, permanganate is safer than salts like cerium and vanadium to human and environment.

The objective of this work is to determine the optimum conditions under which permanganate based coatings can provide good corrosion protection for ZE41 magnesium alloy substrate. The corrosion behavior was studied in 3.5%NaCl solution open to air and at room temperature by means of EIS and cyclic potentiodynamic polarization techniques. Surface examination was performed by SEM-EDS, optical microscopic examination and visual inspection.

2. EXPERIMENTAL

2.1. Materials and surface preparation

Specimens of Mg-Zn-rare earth alloy Elektron ZE41 in the form 30 x 60 x 3mm were cut from a sand cast plate 100 x 200 x 25mm provided by Magnesium Elektron, UK. The specimens were abraded to 800 # finish, degreased, washed, and dried. The alloy chemical composition, as provided by the supplier [2], is Zinc 3.5-5.0%, rare earths 0.8-1.7%, Zirconium 0.4-1.0%, and Magnesium balance.

2.2. Solutions and surface treatment:

The coatings are deposited from aqueous solutions containing potassium permanganate using a very simple spontaneous free immersion processing technology that is very similar to that currently used for the toxic chromate system. A thin layer of manganese oxide conversion coatings is deposited on the magnesium alloy surface by a chemical process. Depositions are achieved in 10 minutes and use commercially available chemical, materials and equipment, making the overall process compatible with industrial operations such as those employed by current aircraft manufacturers.

Solutions used in this work were prepared from potassium permanganate salt with different concentrations. The ZE41 magnesium alloy substrates were treated directly in permanganate solutions at different concentrations namely 0, 5, 10, 15, 25 and 50 g/l at the neutral solution pH for 10 minutes open to air and at room temperature. As-abraded samples (uncoated) were used as a blank.

3. ELECTROCHEMICAL TESTING

3.1. Electrochemical Impedance Spectroscopy (EIS):

EIS technique was used to evaluate the electrochemical behavior of the uncoated (as-polished) and coated magnesium samples in 3.5% NaCl solution open to air and at room temperature for up to seven days. The experimental setting for EIS tests has been described in details elsewhere [30].

3.2. Cyclic potentiodynamic polarization measurements:

Cyclic potentiodynamic polarization measurements of the samples previously immersed for seven days in 3.5% NaCl solution were made at a scan rate of 0.07 mV/s using Autolab PGSTAT 30. The potential was recorded starting from a cathodic potential (-200 mV vs OCP) and be allowed to sweep to anodic potential direction till a sudden shift in the current to the active direction will be observed. At that point the sample will be enforced to sweep again in the cathodic direction. The exposed surface area was 2.54 cm². All curves were normalized to 1 cm².

3.3. Surface characterization:

SEM and EDS were used to examine the surface morphology of the coated samples before and after the immersion in 3.5% NaCl solution. SEM images of the samples that immersed in 3.5% NaCl for seven days, washed with deionized water and then dried and coated with gold to improve the images quality were obtained using a Sanxiao cy-828.900 W. Each analysis was performed three times at different spots using screen analysis at very high magnification covering the all size of the spot.

Macroscopic images were taken using Digital Optical metallographic microscope VHX-100K, KEYENCE, Japan, to investigate the types of corrosion produced on the substrate surfaces after seven days of immersion in 3.5% NaCl solution.

4. RESULTS AND DISCUSSION

4.1. Surface Examination

4.1.1. Visual inspection and macro-images

The effect of permanganate coatings concentration on the corrosion inhibition characteristics of ZE41 magnesium alloy substrates was examined before and after seven days of immersion in 3.5% NaCl solution. Visual inspection and macro-images acquired using a digital camera (Fig. 1) revealed severe localized corrosion for the uncoated as-abraded samples. The average number and size of pits decreased sharply after applying permanganate coatings of diluted concentrations (namely 5 and 10 g/l). Increasing the permanganate concentration above 10 g/l has, generally, an adverse effect on the protection performance of magnesium substrate to localized corrosion (pitting and micro-cracks). The

number and the size of pits (the pitting density) increased dramatically for the samples coated with 15 and 50 g/l permanganate.

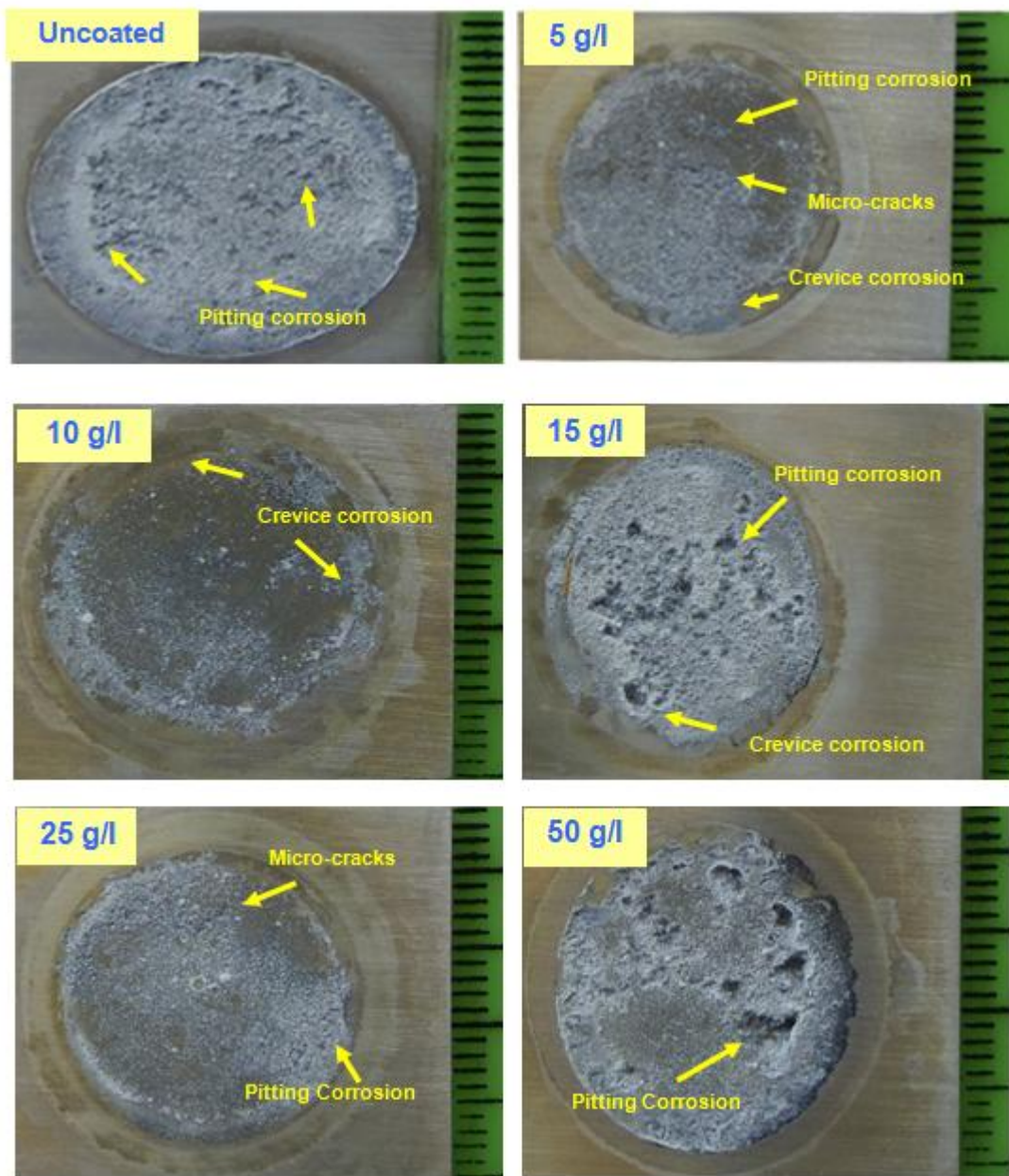


Figure 1. Macroscopic images for ZE41 magnesium alloy substrates coated with permanganate at different concentrations (0 to 50 g/l) after one week of free immersion in 3.5 % NaCl solution.

The number of pits was calculated to be about 8, 2, 1, 11, 2 and 5 pits/cm² for the samples treated in 0, 5, 10, 15, 25 and 50 g/l permanganate solution respectively (Fig. 1). Fig. 2 summarizes the pitting corrosion density of the as-abraded and Mn-coated samples. Although the samples that coated with 5 and 25 g/l permanganate showed noticeable resistances to pitting corrosion, some micro-cracks

and crevice corrosion have been observed. The sample treated in 10 g/l solution showed the best resistance to micro-cracks, crevice and pitting corrosion.

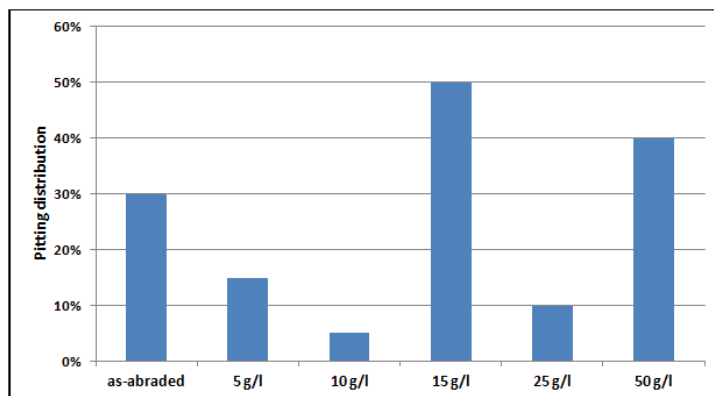


Figure 2. Pitting corrosion density of permanganate coated magnesium samples after one week of immersion in NaCl solution

4.1.2. Optical microscopic images

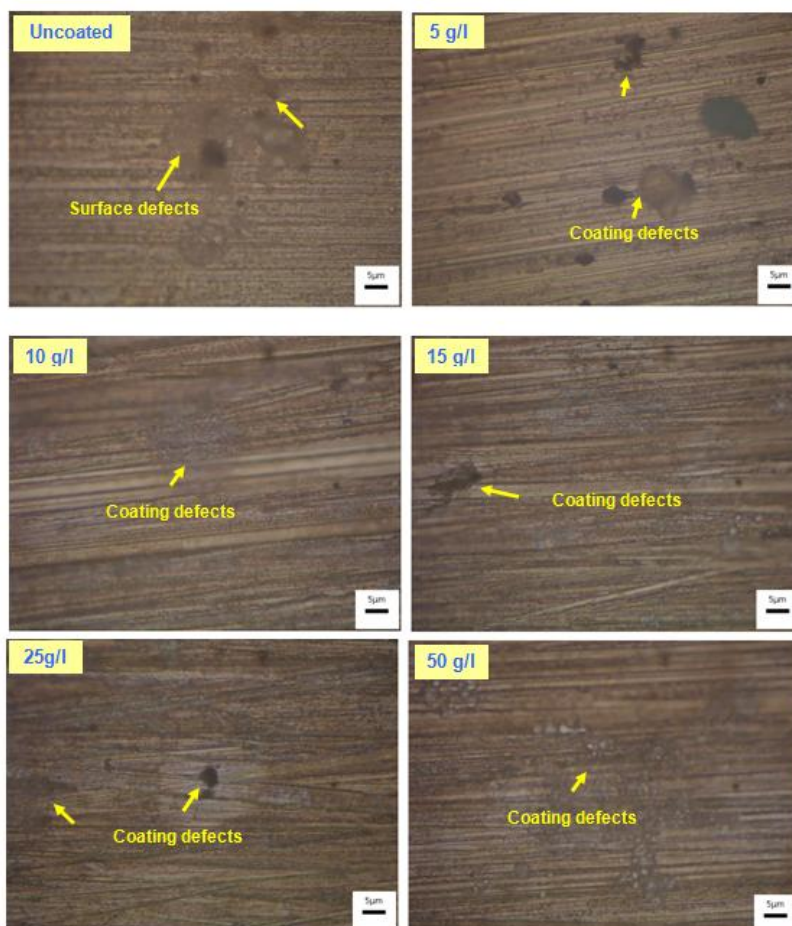


Figure 3. Microscopic images for ZE41 magnesium alloy substrates coated with permanganate at different concentrations (0 to 50 g/l) before corrosion.

Optical microscopy was used to examine the surface and coatings defects, pitting zones and the appearance of the protective film formed at the material surface. Fig. 3 outlines the surface appearance of the as-abraded and Mn-coated samples before corrosion. The samples coated with 10 g/l permanganate solution showed the best smoothness, coating distribution and less defects. Fig. 4 revealed that increasing the permanganate concentration from 0 to 10 g/l resulted in improving the corrosion inhibition characteristics of the coatings. Further increase in the permanganate concentration affects negatively the protective performance of the coatings. The number of pits as well as their morphology (depth and size) decreased sharply in 5 or 10 g/l permanganate coated samples.

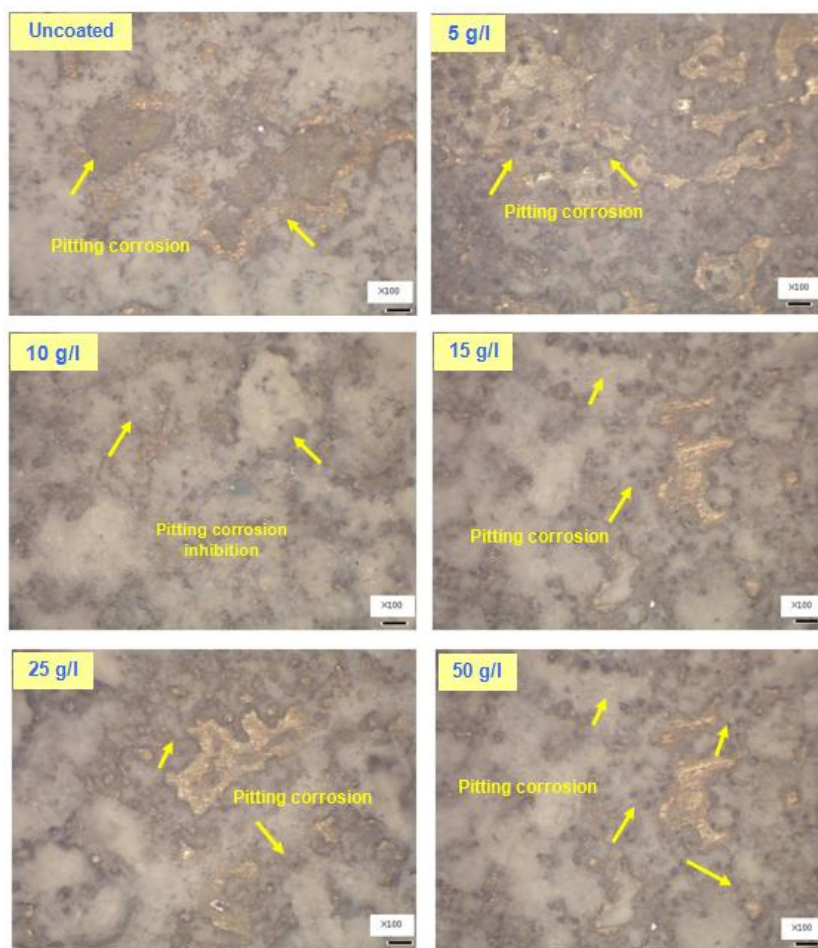


Figure 4. Microscopic images for ZE41 magnesium alloy substrates coated with permanganate at different concentrations (0 to 50 g/l) after one week of free immersion in 3.5 % NaCl solution.

4.1.3. SEM-EDS micrographs

SEM micrograph and EDS microprobe analysis of the uncoated magnesium samples before corrosion in 3.5% NaCl solution revealed formation of rare-earth (Gd and Nd) and zinc oxides in addition to magnesium hydro(oxide) film (Gd, Nd and zinc are present as alloying elements in ZE41 substrates).

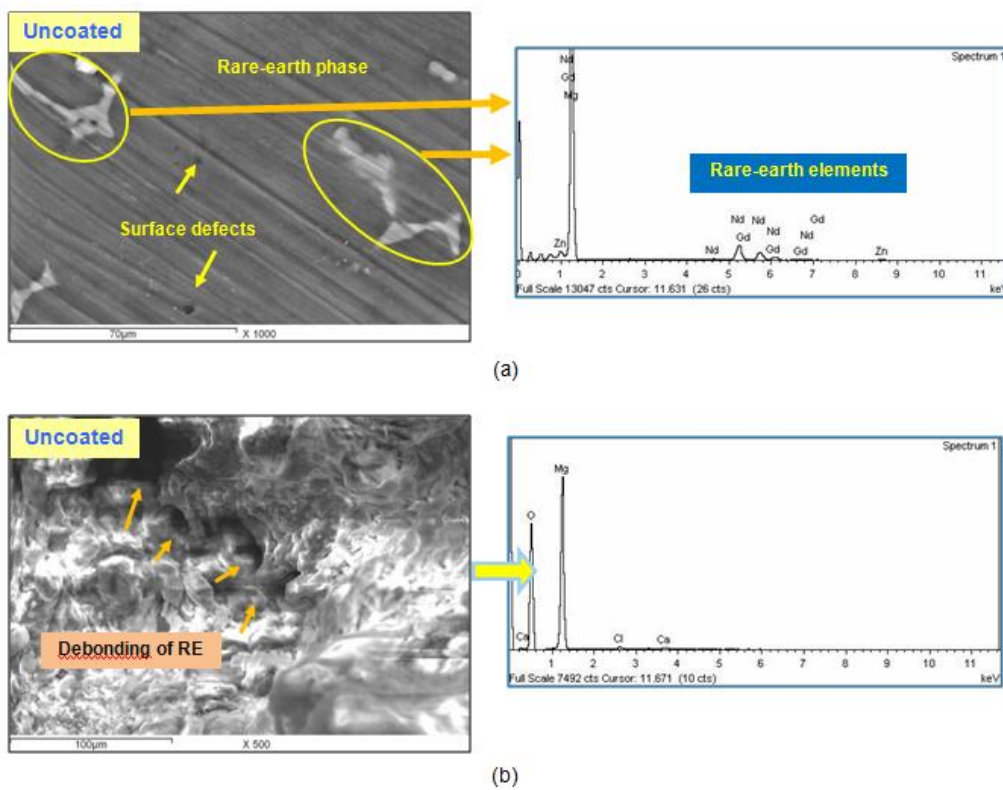


Figure 5. SEM-EDS for the uncoated samples before (a) and after (b) one week of corrosion in 3.5 % NaCl solution.

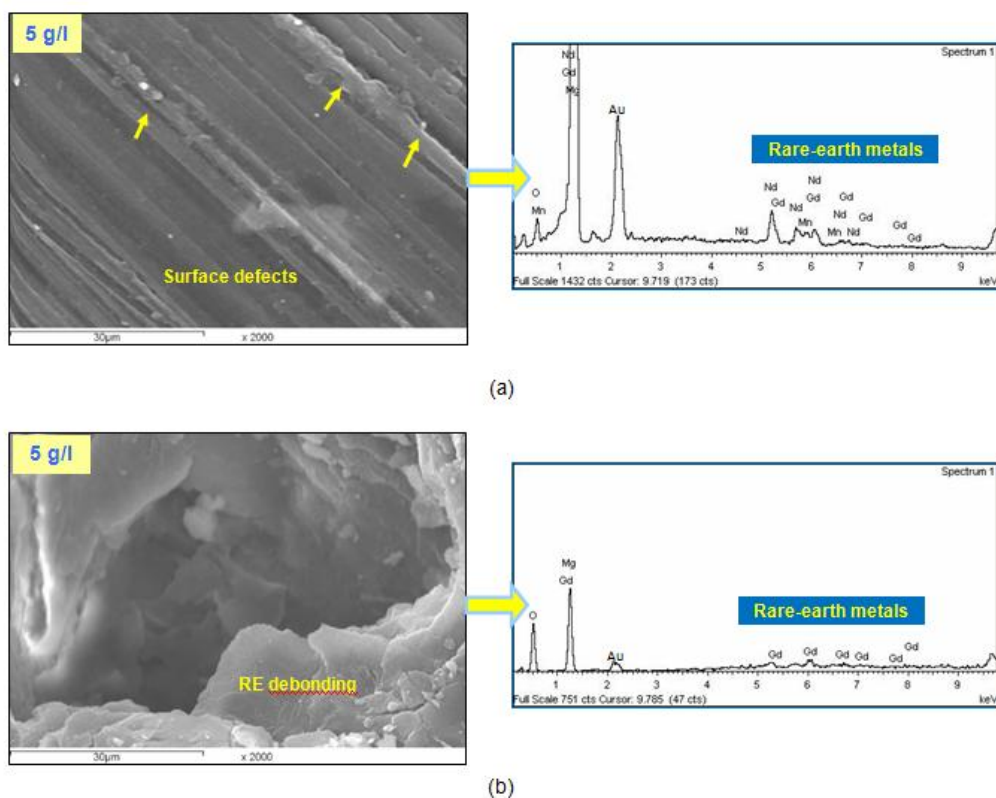


Figure 6. SEM-EDS for the permanganate coated samples at 5 g/l before (a) and after (b) one week of corrosion in 3.5 % NaCl solution.

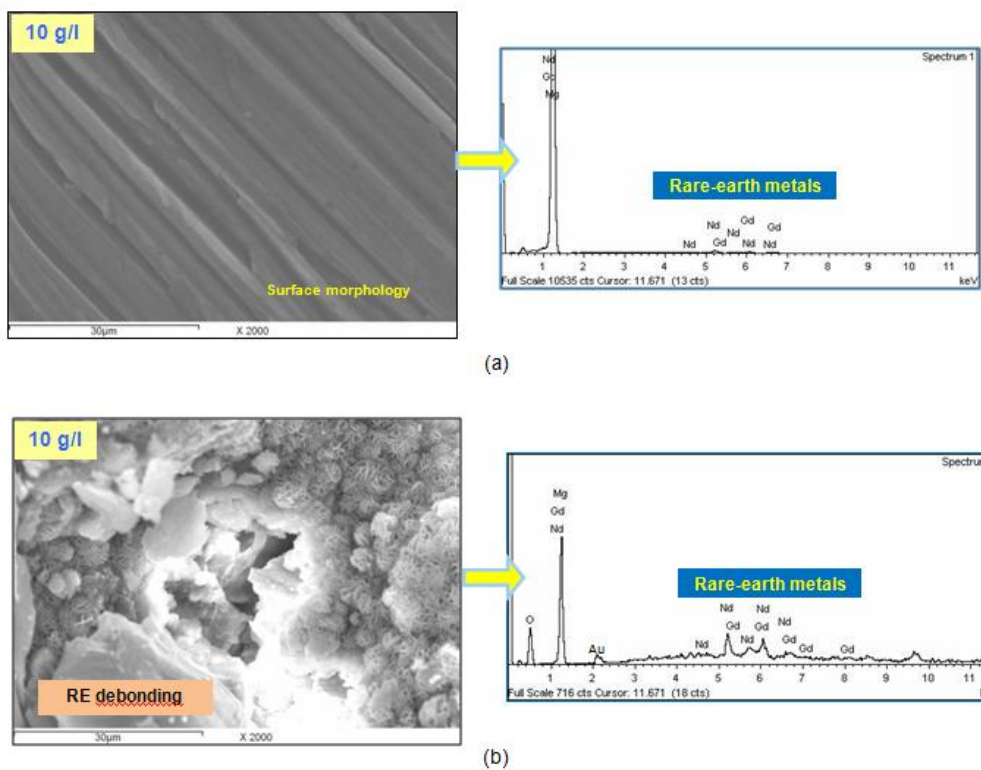


Figure 7. SEM-EDS for the permanganate coated samples at 10 g/l before (a) and after (b) one week of corrosion in 3.5 % NaCl solution.

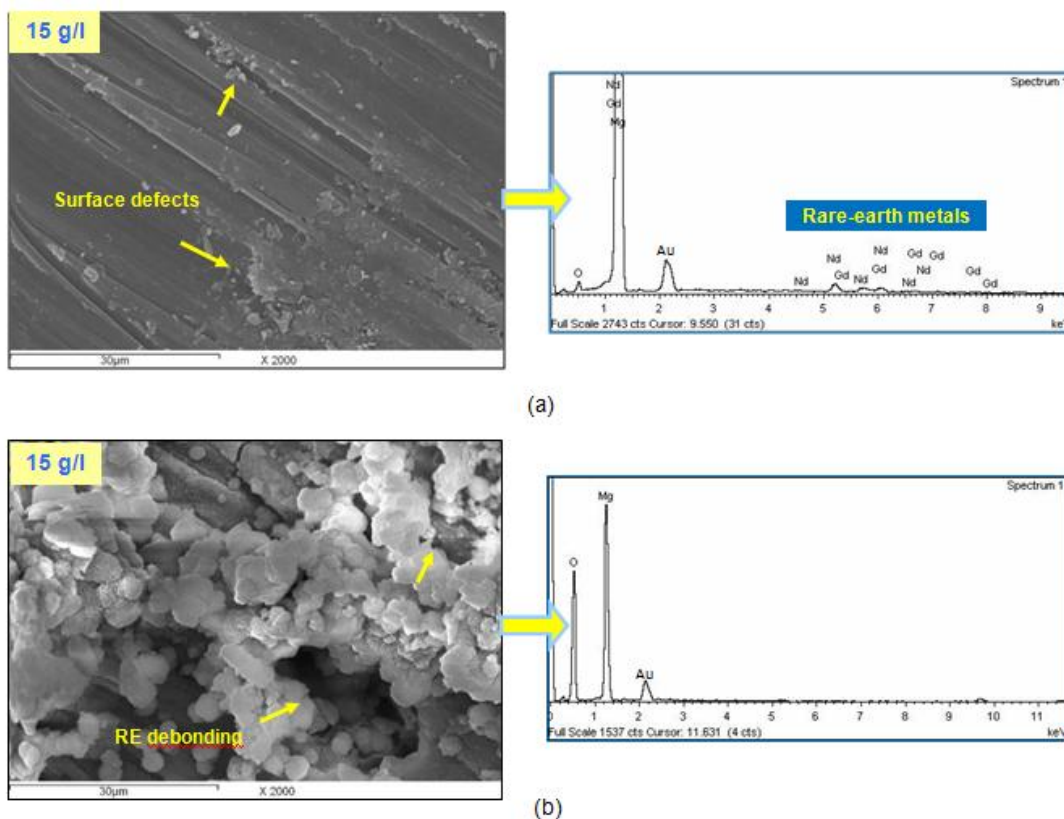


Figure 8. SEM-EDS for the permanganate coated samples at 15 g/l before (a) and after (b) one week of corrosion in 3.5 % NaCl solution.

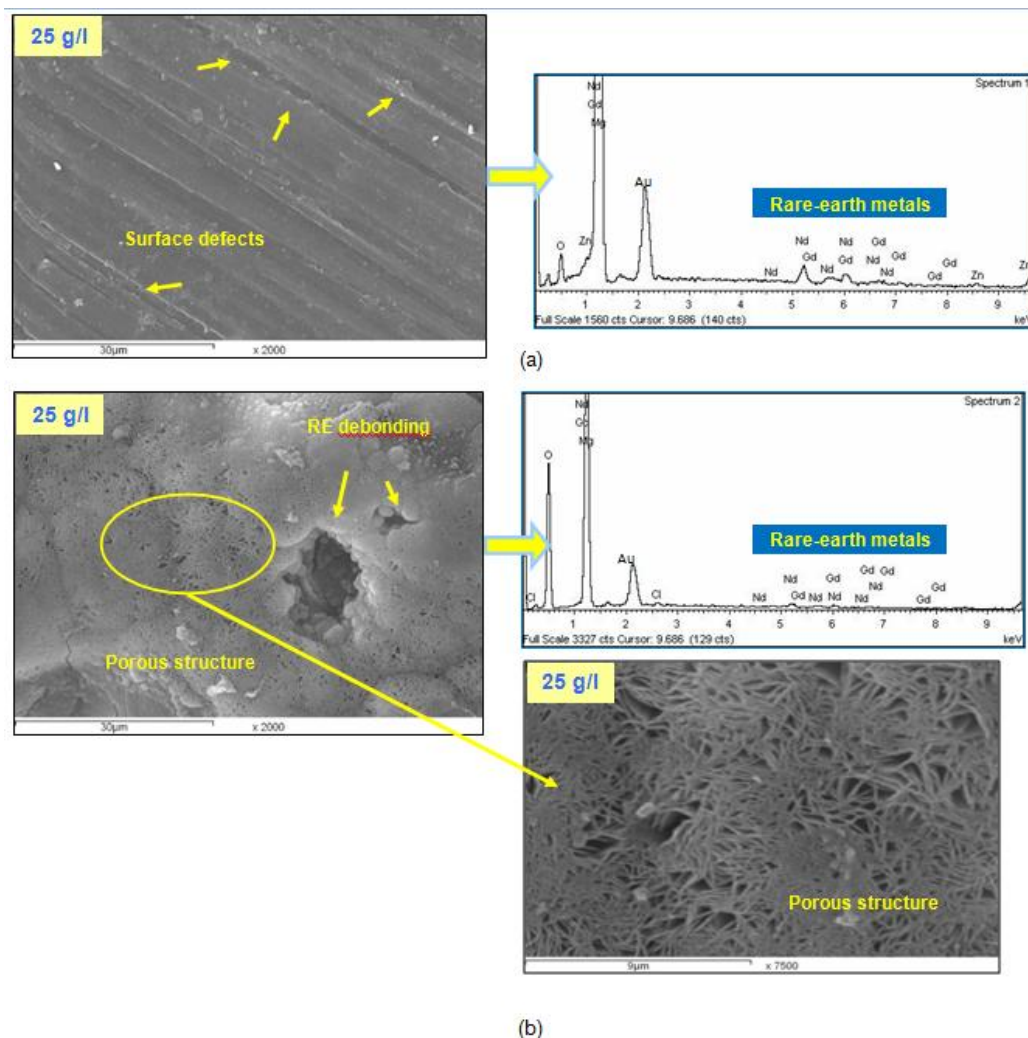


Figure 9. SEM-EDS for the permanganate coated samples at 25 g/l before (a) and after (b) one week of corrosion in 3.5 % NaCl solution.

However, the surface distribution of these oxides formed on the Mg substrate is not uniform and hence, some surface defects which stimulate pitting corrosion on ZE41 alloy upon immersion in NaCl solution were observed [39]. Moreover, the sharp potential difference between the formed rare-earth oxides phases (acts as a cathode) inside the Mg matrix (acts as an anode) results in building up micro-electrochemical cells and enhancing galvanic corrosion. Upon immersion in corrosive chloride solution, the galvanic corrosion propagate and enhance intergranular corrosion around the rare-earth phases. At the end, the rare-earth phase can debonding from the matrix and leaves a hole. In fact, These holes can make a big confusion under the microscopic examination because they appear like pitting corrosion (Fig. 5).

After permanganate treatment, it was expected that a film of Mn-rich magnesium hydro(oxide) be formed. However, XRD was not able to detect the presence of Mn, in all cases, which confirms that the film formed is relatively thin and out of the accuracy limits of the X-ray which needs to be detected by more sensitive techniques such as XPS. SEM micro-image showed that the film formed due to 10 g/l permanganate treatment is the best among the other concentrations in terms of the coating

distribution and surface morphology (Figs 6-10). Unexpectedly, the presence of Mn was not detected by microprobe analysis using EDS for all the samples except those coated with 5 g/l.

When immerse the permanganate coated samples in corrosive 3.5% NaCl solution, the samples coated with diluted permanganate (5 and 10 g/l) showed a distinct reduction in the number and the size of pits and holes as shown in Figs. 6 and 7. Conversely, the samples coated with 15 and 50 g/l showed severe pitting, crevice corrosion and intergranular attack (Figs. 8 and 10). The samples coated with 25 g/l permanganate showed a relative improvement in pitting corrosion resistance. However, it was found that the film formed is porous and some areas of micro-cracks have been detected. Based on these findings, treatment of ZE41 substrates with the diluted permanganate solution (5 and 10 g/l) offers better resistance to pitting, galvanic and intergranular corrosion than other permanganate concentrations. However, the samples treated with 5 g/l permanganate showed few holes (Fig. 6) which is not the case with 10 g/l permanganate coated samples. Accordingly, the best surface protection efficiency can be achieved by a one-step surface treatment in 10 g/l permanganate solution (Fig. 7).

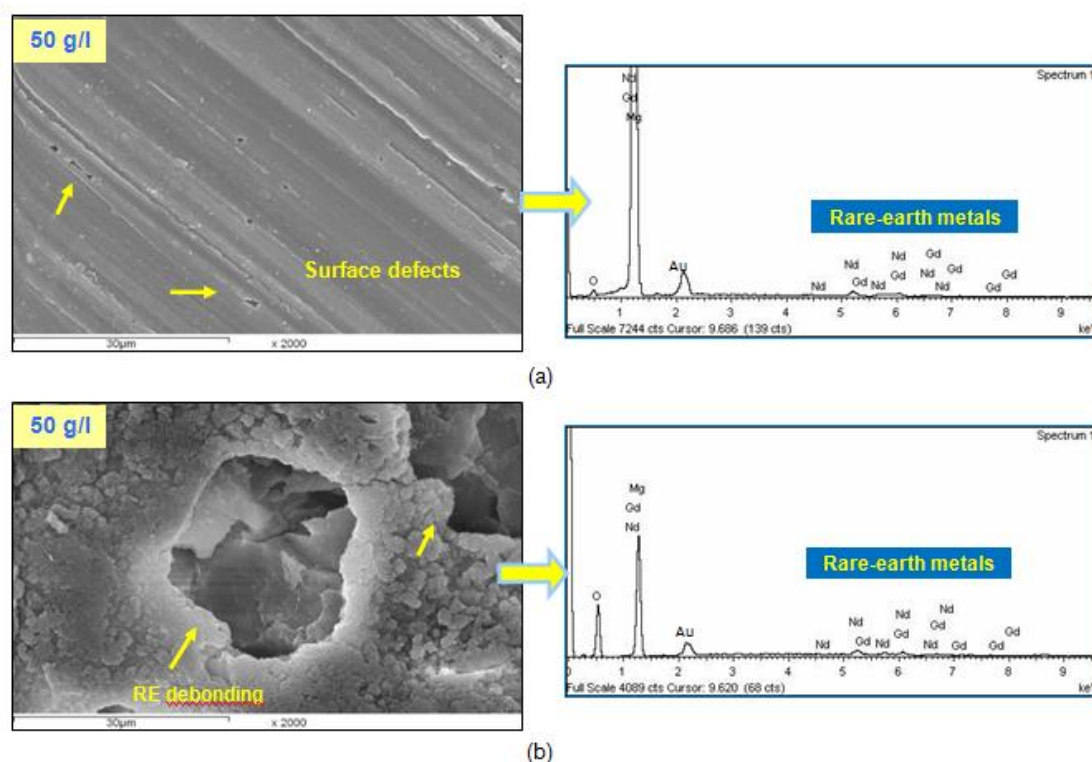


Figure 10. SEM-EDS for the permanganate coated samples at 25 g/l before (a) and after (b) one week of corrosion in 3.5 % NaCl solution.

4.2. Electrochemical impedance spectroscopy:

The surface resistance of ZE41 magnesium alloy substrates before and after permanganate treatment at different concentrations ranging from 0-50 g/l has been evaluated in 3.5% NaCl solution.

According to Nyquist plots (Fig 11a), the corrosion resistance of the ZE41 magnesium alloy substrates improved with permanganate surface treatment at low concentration (5 and 10 g/l). Increasing the permanganate concentration up to 10 g/l has an adverse effect on the localized corrosion resistance.

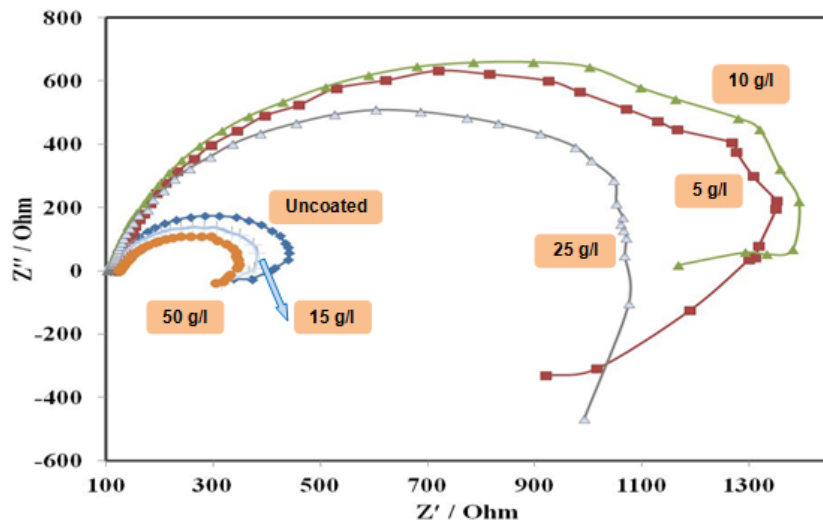


Figure 11a. Nyquist plots for uncoated and permanganate coated magnesium samples (different permanganate concentrations) after one week of immersion in 3.5 %NaCl solution

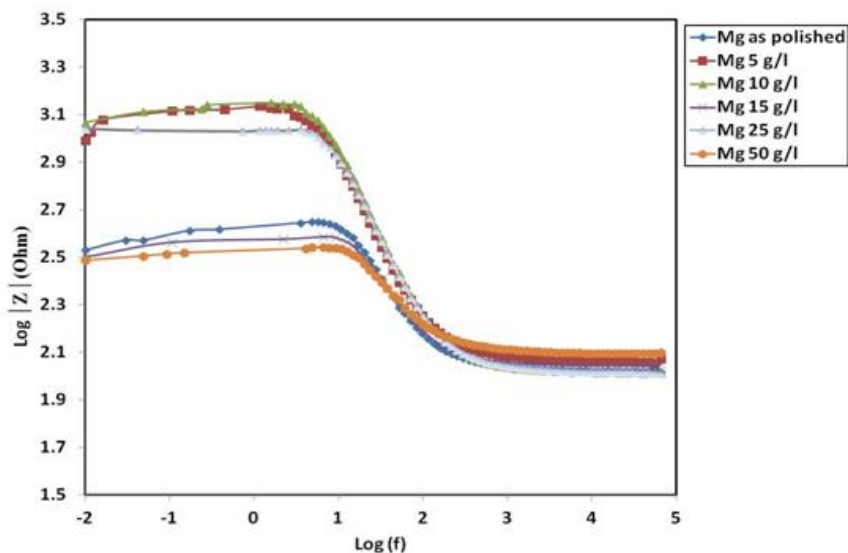


Figure 11b. Resistance spectra of Bode plots for uncoated and permanganate coated magnesium samples (with different permanganate concentrations) after one week in 3.5 %NaCl solution

As-abraded samples showed a surface resistance of approximately $0.45 \times 10^3 \Omega \cdot \text{cm}^2$ after one week of immersion in corrosive 3.5% NaCl solution. The surface resistance improved almost three folds for the samples coated with 5 and 10 g/l permanganate. The surface resistances values were 1.35×10^3 and $1.43 \times 10^3 \Omega$ for the samples coated with 5 and 10 g/l permanganate respectively as

measured by EIS. Increasing the permanganate concentration more than 10 g/l proved to have an adverse effect of the surface resistance of ZE41 alloy in chloride containing solution. The surface resistances decreased to be 0.38×10^3 , 1.05×10^3 and $0.35 \times 10^3 \Omega$ for the samples coated with 15, 25 and 50 g/l permanganate respectively. Accordingly, the samples coated with 10 g/l permanganate showed the best surface protection which confirm the previous results of visual inspection, macro-image, and SEM-EDS.

The resistance spectra in Bode plots (Fig. 11b) provide further explanation of these observations where the samples treated in diluted permanganate solutions (5 and 10 g/l) showed the highest polarization resistance (R_p) compared with the as-abraded samples and the samples coated with concentrated permanganate solution (15, 25 and 50 g/l). The resistance values of the diluted permanganate coated samples reflect good barrier properties, associated with the impediment of the electrolyte to reach the metallic substrate due to the formation of the permanganate-rich magnesium hydro(oxide) film over the substrate.

The permanganate coating prepared in 10 g/l solution promotes the increasing of the low frequency impedance by almost one order of magnitude compared to the as-abraded Mg alloy and other permanganate coating conditions. The reduction of impedance reveals the deterioration of the protection system. The resistance and capacitance values associated with the permanganate coating prepared in 10 g/l solution reflect good barrier properties, associated with the impediment of the electrolyte to reach the metallic substrate.

According to the impedance spectra (Fig. 11a and b), coating of ZE41 magnesium alloy substrates with 10 g/l permanganate improves the localized corrosion resistance which attributed to the formation of the protective Mn rich oxide film which prevents the oxygen diffusion to the metal surface and therefore, impede corrosion but not prevent it as confirmed by surface examination.

4.3. Cyclic potentiodynamic polarization:

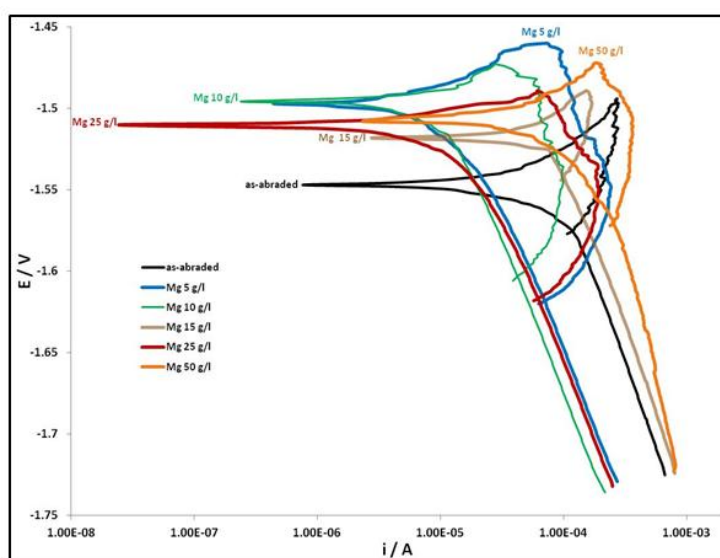


Figure 12. Cyclic potentiodynamic polarization curves for uncoated and permanganate coated magnesium samples (different permanganate concentrations) after one week of immersion in 3.5% NaCl solution

Cyclic potentiodynamic polarization (Fig. 12) confirmed the previous results obtained from EIS and surface examinations in terms of occurrence the localized corrosion where the cathodic current was shifted from 2×10^{-3} A for uncoated specimens to be 8×10^{-3} A for 5 and 10 g/l permanganate coated samples. The corrosion potential, E_{Corr} , of the 5 and 10 g/l permanganate samples is -1.49 V which is more noble than the uncoated samples (-1.55 V). The pitting potential can be determined by the point at which a sudden shift in the current can be observed. The pitting potential, E_{pit} , of the 5 and 10 g/l permanganate samples is -1.46 and -1.47 V respectively higher than the pitting potential of uncoated samples (-1.55 V). However, the pitting loop, which represents the chance of pitting corrosion to occur, is smaller in the 10 g/l permanganate samples compared with the 5 g/l permanganate. The presence of some tiny pits for the 5 and 10 g/l permanganate samples can be attributed to the presence of some coatings defects. This film behaves as a barrier to protect the material substrate from the reaction with dissolved oxygen in NaCl solution and hence impedes the localized corrosion by shifting the cathodic reaction to more noble current and shifting the anodic reaction to more noble potential.

The main advantage of the new permanganate surface treatment approach proposed in this paper is the simplicity of the coating process compared with several high performance coatings technology recently investigated in the literatures which imply several coatings steps and several coating layers [9, 40-43]. Another advantage is the safety of permanganate to environment and coatings workers compared with the process involving toxic chromate.

5. CONCLUSION

1- Rare-earth containing ZE41 magnesium alloy possesses unique mechanical properties as a promising material for transportation industry. However, It was noticed that the sharp potential difference between the formed rare-earth phases (cathode) inside the Mg matrix (anode) results in building up micro-electrochemical cells and enhancing galvanic corrosion. Upon immersion in chloride solution, the galvanic corrosion propagates and enhances intergranular corrosion around the rare-earth phases. At the end, the rare-earth phase can debond from the matrix and leaves a hole.

2- A new simple approach for designing chrome-free coatings based on permanganate surface treatment for improving the corrosion resistance of rare-earth-ZE41 magnesium alloy in chloride containing environment has been discussed.

3- A one-step coating formed by simple free immersion in a diluted permanganate solution for quite short time (10 min) was found promising to increase the corrosion protection of ZE41 magnesium alloy substrates.

4- According to the surface examination, electrochemical impedance spectra and cyclic potentiodynamic polarization measurements, 10 g/l permanganate is the optimum permanganate coating concentration that offers the best corrosion protection to the Mg substrate in NaCl solution.

5- It was proven that permanganate coating improves the corrosion inhibition characteristics of ZE41 magnesium alloy substrates by forming a manganese-rich oxide film over the pitting areas.

6- The permanganate coatings proposed in this study would be only a first pre-treatment (primer) film to ZE41 magnesium alloy substrates, and a final top coat will be crucial to reach an adequate corrosion protection.

References

1. M. K. Kulekci, *The International J. Advanced Manufacturing Technology*, 39, 9-10 (2008) 851.
2. <http://www.magnesium-elektron.com/data/downloads/452A.pdf>
3. P.L. Hagans and C.M. Haas, *ASM Handbook*, Vol. 5, Surface Engineering, 10th Ed., F. Reidenbach, 1994, Metals Park, OH, ASM International, p. 405.
4. M. Kendig and R.G. Buchheit, *Corrosion*, 59, 5 (2003) 379.
5. M. Kendig and C. Yan, *J. Electrochem. Soc.*, 151, 12 (2004) B679
6. M. Koudelkova, J. Augustynski and H. Berthou, *J. Electrochem. Soc.*, 124, 8 (1977) 1165
7. P.G. Sheasby and R. Pinner, *The Surface Treatment and Finishing of Aluminum and its Alloys*. Vol 1, 2001, Materials Park, OH, ASM International, Ch 5, p.231.
8. G.S. Frankel and R.L. Mccreery, *Electrochem. Soc. Interface*, 34 (2001) 13.
9. D. Seifzadeh and A.G. Haghghat, *Indian J. Chemical Technology (IJCT)*, 20, 3 (2013) 210.
10. R.G. Buchheit, ECS PV2002-13, Pennington, NJ, 430, (2002)
11. P. Campestrini, G. Goeminne, H. Terryn, J. Vereecken, *J. Electrochem. Soc.*, 151, 2 (2004) B70,
12. J.S. Crompton, P.R. Andrews and E.M. Alpine, *Surf. and Int. Anal.*, 13 (1988) 160.
13. C.S. Jeffcoate, H.S. Isaacs, A.J. Aldykiewicz, and M.P. Ryan, *J. Electrochem. Soc.*, 147, 2, (2000) 540.
14. B.L. Hurley and R.L. Mccreery, *J. Electrochem. Soc.*, 150, 8 (2003) B367.
15. H. Ardeean, I. Frateur, P. Marcus, *Corrosion Science*, 50, 7 (2008) 1907.
16. P. Marcus, H. Ardelean, Patent PCT/FR 02/01843, WO 02/097164 A2, 2002, US Patent 7 156 905, 2007.
17. H. Ardelean, I. Frateur, S. Zanna, A. Atrens, P. Marcus, *Corrosion Science*, 51, 12 (2009) 3030.
18. K. Z. Chong, T. S. Shih, *Materials Chemistry and Physics*, 80, 1 (2003) 191.
19. M. Takaya, *Jpn. Inst. Light Met.*, 45,12 (1995), 713.
20. H. Umehara, M Takaya, Y Kojima, *Mater. Trans. JIM*, 42, 8 (2001) 1691.
21. D. Y. Hwang, Y. M. Kim, D-Y Park, B. Y. Yoo, D. H. Shin, *Electrochimica Acta*, 54, 23 (2009) 5479.
22. D. Y. Hwang, K-R. Shin, B. Yoo, D-H. Lee, D-Y. Park, D-H. Shin, *Trans. Nonferrous Met. Soc. China*, 19 (2009) 829.
23. A.S. Hamdy (Editor): "High Performance Coatings for Automotive and Aerospace Industries", Nova Science Publishers, NY, USA, ISBN: 978-1-60876-579-9, 2010.
24. A.S. Hamdy and I. Tiginyanu (Editors), "Nanocoatings and Ultra Thin-Films", Woodhead Publishing Limited, UK, ISBN: 978-1-84569-812-6, 2011.
25. A.S. Hamdy (Editor): "Handbook of Smart Coatings for Corrosion Protection", Woodhead Publishing Limited, UK, in press.
<http://www.woodheadpublishing.com/en/book.aspx?bookID=2745>
26. A. S. Hamdy, *J. Anti-Corrosion Methods and Materials*, 53, 6 (2006) 367.
27. A.S. Hamdy, *J. Electrochemical and Solid-State Letters*, 10, 3 (2007) C21-C25.
28. A.S. Hamdy, *European Coatings Journal*, 86, 3 (2008) 43.
29. A. S. Hamdy, *J. Surface Coatings and Technology*, 203 (2008), 240
30. A.S. Hamdy, and M. Farahat, *J. Surface and Coatings Technology*, 204 (2010) 2834.
31. A.S. Hamdy, I. Doench, and H. Möhwald, *J. Electrochimica Acta*, 56 (2011) 2493.
32. A.S. Hamdy, I. Doench, and H. Möhwald, *Progress in Organic Coatings*, 72 (2011) 387.
33. A.S. Hamdy, I. Doench, and H. Möhwald, *J. Thin Solid Films*, 520 (2011), 1668.

34. A.S. Hamdy, I. Doench, and H. Möhwald, *J. Materials Science (JMSC)*, 47, 8 (2012), 3784.
35. A.S. Hamdy, *European Coatings Journal*, 3 (2012), 16.
36. A.S. Hamdy, I. Doench, and H. Möhwald, *Surface Coatings & Tech.*, 206, (2012), 3686.
37. A.S. Hamdy, I. Doench, and H. Möhwald, *Int. J. Electrochemical Science*, 7, (2012), 7751.
38. A.S. Hamdy and D. Butt, *J. Electrochimica Acta*, (2013), 296.
39. A.S. Hamdy and H. Hussien, "A one-step environmentally safe permanganate-based coating treatment for ZE41 Mg-Zn-rare earth alloy in chloride media", *Int. J. Electrochemical Science*, in review.
40. J. Bibber, Corrosion resistant magnesium and magnesium alloy and method of producing same, US 20040115448 A1, 2004.
41. J. I. Skar, and D. Albright, Phosphate Permanganate: A Chrome Free Alternative for Magnesium Pre-treatment, in *Magnesium Alloys and their Applications* (ed K. U. Kainer), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG. doi: 10.1002/3527607552, ch75 (2006)
42. J. Tkacz, A. Němcová, M. Zmrzlý, B. Pacal, *Koroze a ochrana materiálu*, 56, 4 (2013) 100.
43. Y.L. Lee, Y.R. Chu, W.C. Li, C.S. Lin, *Corrosion Science*, 70 (2013) 74