Stability of Permanganate Conversion Coating Formed on ZE41- Mg Alloy at Different pHs and Coating Times

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Abstract

The corrosion resistance of the permanganate conversion coating formed on ZE41- Mg alloy as affected by coating time and pH was studied by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and polarization methods in order to find the optimum treatment conditions. The morphology of the coated and uncoated (as-abraded) samples was analyzed with scanning electron microscope (SEM), energy dispersive X-ray (EDX) and X-ray diffraction (XRD). All corrosion tests and surface analysis were done before and after immersion in corrosive (3.5% NaCl) solution. The obtained results demonstrated that the corrosion resistance of the coated samples in neutral and acidic solutions was significantly higher than that of as-abraded alloy in the studied solutions. In addition, the results declared that the best corrosion resistance was recorded in permanganate solution of pH 7.5 at coating time 10 min.

Keywords: Magnesium alloy, Conversion coating, Corrosion resistance, Permanganate treatment.

INTRODUCTION

Nowadays, magnesium alloys are increasingly used in a lot of applications where a reduction of weight without a loss in stability is required. Furthermore, they are very promising materials for the transportation sector owing to the actual urge in the modern society for new cleaner vehicles which can provide the same comfort and performance of the traditional ones but in a much greener and economic manner [1].

A series of magnesium alloys, containing a minor percentage (0.8-1.7%) of rare-earth (RE) elements, such as ZE41 has been designed by Magnesium Elektron [2]. The corrosion resistance of these magnesium alloys strongly depends on the alloying elements, alloy processing and on the impurities level. However, it has been reported that the corrosion resistance of ZE41 is relatively low [2]. Recently the corrosion resistance of magnesium alloys can be enhanced using conversion coating produced by chemical or electrochemical treatment

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includes immersing the metal in a solution containing certain compounds. These compounds react by forming superficial films of substrate metal oxides, chromates, phosphates or other compounds. The films are then chemically bonded to the metal surfaces [3,4].

Due to the environmental regulations, chromate coating methods may not be used anymore. So different conversion coatings based on eco-friendly salts such as permanganate [5], molybdate [6-8], phosphate [4], cerate [3], stannate [3, 9-11],...etc, have been proposed as alternatives to the process involving toxic hexavalent chromate. Many researchers [5,10,12-16] studied different types of permanganate conversion coating treatment on different types of Mg alloys and the results indicated that the corrosion resistance of the coated samples is significantly higher than that of the uncoated ones.

However, the higher cost of the existing coating methods or the multi-step coatings with long treatment times, in addition to the involving of relatively complicated procedures for formation of complex coatings with more than one oxide of elements are considered the main challenges to use such coatings [17]. Therefore, provision of eco-friendly, cost-effective, industrially-applicable coating technologies, with ready application to magnesium alloys in the transportation sector, are at the motives of this work.

ZE41 is a magnesium casting alloy of medium strength which is ideal for high integrity casting and operating at ambient temperatures. Moreover, 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. On the other hand, permanganate salts have many advantages over most of the other salts used before in chrome-free coatings manufacturing. They are quite cheap compared with cerium, vanadium, zirconium, and stannate salts. Moreover, permanganate is safer than salts of cerium and vanadium to human and environment [17].

The objective of this work is designing of a high performance environmentally-friendly permanganate surface treatment of optimized pH and treatment time that can be used as a primer prior to a final top coating for ZE41- Mg alloy substrate.

EXPERIMENTAL

Materials and surface preparation

Specimens of Mg-Zn-rare earth alloy Elektron (ZE41- Mg alloy) in the form 30 x 60 x 3 mm 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 in acetone, washed with distilled water, and dried in dry air. The chemical composition of alloy, as provided by the supplier [2], is Zn 3.5-5.0%, rare earths (Nd and Gd) 0.8-1.7%, and Magnesium balance.

Solutions and surface treatment

Potassium permanganate with 10 g/l concentration as coating solution and 3.5% NaCl as corrosive solution were prepared using bi-distilled water. This specified permanganate concentration was recommended by previous work as it was examined among series of different concentrations and 10 g/l gave the best corrosion resistance of this alloy [17]. The effect of changing the permanganate coating time, namely at 5, 10 and 20 min, was investigated in neutral coating solution of pH 7.5. After getting the time which gave the best coating properties, the ZE41- Mg alloys were treated directly in permanganate solutions at different pHs, namely pH 5.5, 7.5 and 9.5. The pH of the solution was adjusted by adding few drops of 0.1 M HNO$_3$ for acidic medium and 0.1 M NaOH for alkaline medium. In the two testing variables, as-abraded samples (uncoated) were used as a blank. After coating, the samples were suspended to corrosion in 3.5% NaCl solution for one week (open to air at room temperature) before testing the surface properties.

The coating process was done using commercially available chemicals, materials and equipments, making the overall process compatible with industrial operations such as those employed by current aircraft manufacturers.

Testing techniques

All electrochemical tests were done on ZE41- Mg alloys of 2.54cm^2 exposed surface areas using an electrochemical analyzer instrument: (Autolab PGSTAT 30). A saturated calomel electrode (SCE) was used as the reference electrode which was coupled capacitively to a platinum wire. All curves were normalized to 1 cm^2.

Electrochemical impedance spectroscopy (EIS)

EIS technique was used to evaluate the electrochemical behavior of the uncoated and coated samples of ZE41- Mg alloys after immersion in corrosive 3.5% NaCl solution for one week open to air. The experiments were performed at room temperature over the frequency range between 0.01 Hz and 65 kHz at open circuit potential. The amplitude of the sinusoidal voltage signal was 10 mV.

Cyclic Voltammetry measurements (CV)

Cyclic polarization measurements of Mg- samples previously immersed for one week in 3.5% NaCl solution were made at a scan rate of 0.07 mV/s. The potentials were starting from a cathodic potential (-200 mV vs open circuit potential) and be allowed to sweep to anodic direction till a sudden shift in the current to the active direction is observed. At that point the potential is enforced to sweep again in the cathodic direction.

Linear polarization

In linear polarization, each specimen was polarized from −30 to +20 mV with regard to the open circuit potential, at scanning rate equals to 0.07 mV/s, to study the polarization resistance (R_p). Values of corrosion current densities (I_{corr}) and corrosion potential (E_{corr}) were determined from the extrapolation of linear segments of anodic and cathodic curves. The corrosion rate (C_R) in mpy was calculated using the following equation [18]:

$$C_R = 0.13 \times I_{corr} \times e/\rho \qquad (1)$$

where 0.13 is the metric and time conversion factor, I_{corr}, is the corrosion current density in $\mu A/cm^2$, e is the equivalent weight of alloy in geq/mol and ρ, is its density in g/cm^3.

Surface characterization

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 immersion in 3.5% NaCl solution.

SEM and EDX were used to examine the surface morphology of the coated samples before and after immersion in 3.5% NaCl solution using a Sanxiao cy–828.900 W. The samples were washed with deionized water, dried and coated with gold to improve the images quality.

It is worth to mention that each analysis was preformed three times at different spots using screen analysis at very high magnification covering all size of the spot.

RESULTS AND DISCUSSION

Electrochemical impedance spectroscopy

Coating time had a great importance in industrial applications. Thus, the corrosion resistance of ZE41– Mg alloy coated for 5, 10 and 20 min in neutral permanganate solution at pH 7.5 and compared with as– abraded sample was evaluated after one week immersion in 3.5% NaCl solution. According to Nyquist plots (Figure 1), the samples that coated for 10 min showed the highest resistance and capacitance values. Moreover, it is evident from Figure 1 that the semicircle diameter decreased in the following order:

10 min > 20 min > as–abraded > 5min.

Since the diameter of the capacitive semicircle represents the resistance of the coatings, the resistance decreases significantly with the decrease in diameter [3]. This indicated that the corrosion resistance of ZE41– Mg alloy coated for 10 min in permanganate solution was the greatest of all treatment times. Furthermore, an inductive loop was observed at 5 min coating time which was attributed to the occurrence of pitting corrosion induced by chloride anions in corrosive solution because the magnesium alloy surface cannot be covered by the permanganate conversion coating completely at this time. Thus, a destruction of the coated

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layer as a result of permeation of chloride ions from salt water into the coating causes the dropping in resistance and capacitance from that at zero time (as-abraded) to lower values. Similar results were reported by Yong Zhou *et al.* [4] that the coated magnesium alloys with low immersion time are composed of a capacitive loop at high frequency and an inductive loop at low frequency region of EIS.
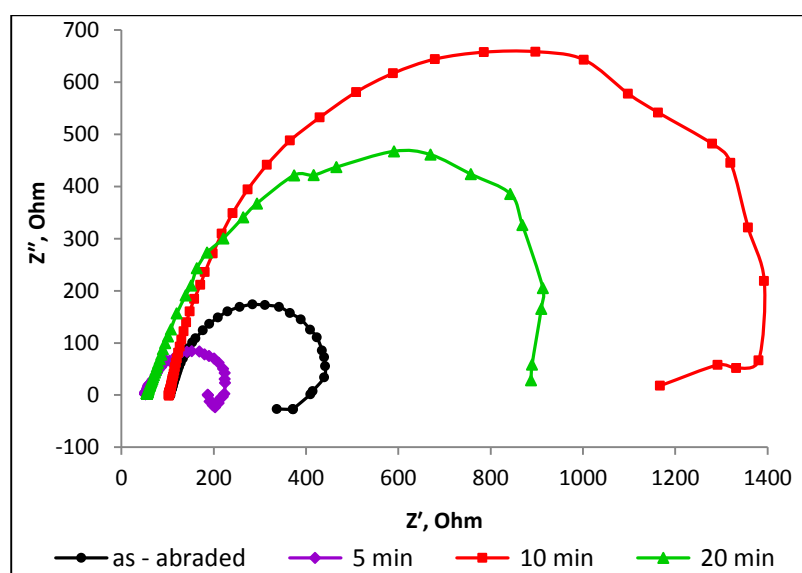

Figure 1: Nyquist plots of permanganate coated ZE41- Mg alloy at different treatment times after one week of immersion in 3.5% NaCl solution.

Concerning the effect of changing the pH of the coating solution on the corrosion resistance of ZE41- Mg alloy immersed in corrosive 3.5% NaCl solution, the corrosion resistance was tested at pH 5.5, 7.5, 9.5 and compared with the as-abraded sample at the optimum coating time, 10 min, since it was recorded as the best time to get the maximum protection. According to Nyquist plots (Figure 2-a), the best resistance and capacitance values were obtained for the samples coated with permanganate at pH 7.5 which was characterized with wide large semicircle compared with that of other solutions. This indicated that the thickness of the permanganate conversion coating grown at pH 7.5 was thicker than that grown at other pH media. Similar behavior was observed by Zhou *et al* and Cheng *et. al.*[4, 19] in their study of a phosphate conversion coating on AZ91D- Mg alloy. Moreover, coating with permanganate showed better resistance in neutral and acidic media when compared with as-abraded sample. However, coating in alkaline media had an adverse effect when immersed in
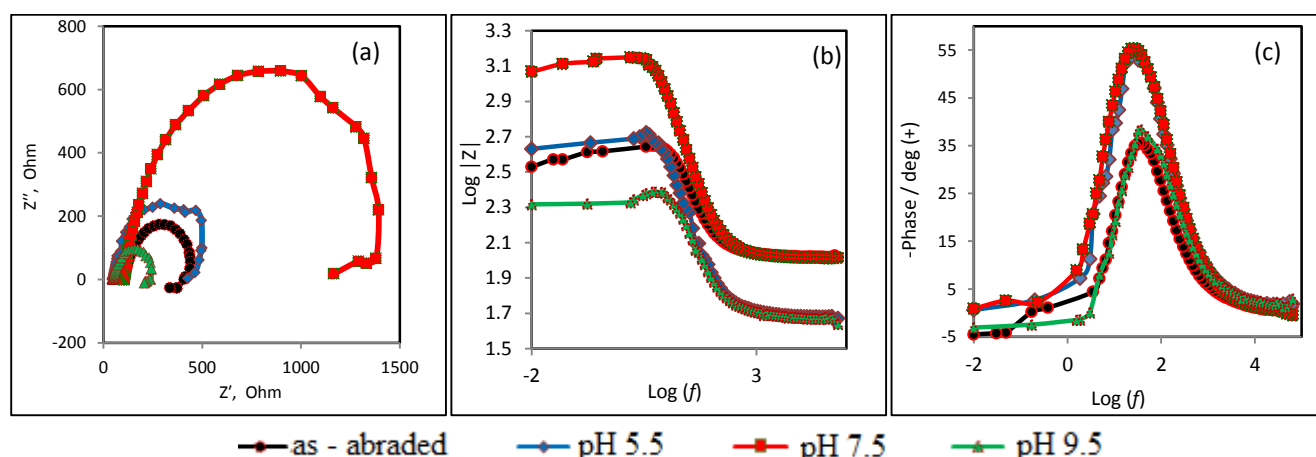
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Figure 2: EIS spectra for as–abraded and permanganate coated magnesium samples at different pHs after one week of immersion in 3.5% NaCl solution: (a) Nyquist plots, (b) Bode–magnitude plots, (c) Bode–phase angle plots.

corrosive solution which might be attributed to the localized dissolution of the permanganate conversion coating in the chloride media.

By using Bode plot format, the logarithmic values of absolute impedance (|Z|) vs. frequency (f) of coated ZE41–Mg alloy immersed for a week in chloride media showed a linear variation (Figure 2–b) which referred to the capacitive behavior. The different impedance parameters are tabulated in Table 1.

The surface resistance (impedance (Z)) recorded for as–abraded sample was 426 $\Omega.cm^2$ (Table 1). The surface resistance was improved more than three folds for the samples coated with permanganate at pH 7.5. The impedance values decreased sharply for the other samples. The reduction of impedance (Z) revealed the deterioration of the protection system due to localized corrosion [17]. The polarization resistance (R_p) represents the dissolution resistance of the passive film. The highest value of R_p was recorded for magnesium alloy in permanganate solution of pH 7.5. Also, values of R_e, which represent the resistance of the electrolyte between the working and the reference electrode, reached its highest value in permanganate solution of pH 7.5. For all solutions under study, the phase angle θ did not reach a value of 90° (Figure 2–c and Table 1), which is an indication of a non–ideal capacitive behavior.

In a nutshell, the optimum pH of coating permanganate solution to get the maximum corrosion resistance of ZE41–Mg alloy was pH 7.5 followed by pH 5.5 then as–abraded alloy. The lowest corrosion resistance was observed when Mg– alloy was coated at permanganate solution of pH 9.5.

Table 1: Impedance parameters for as-abraded and coated ZE41- Mg alloy at different pHs of permanganate coating solution

	Z	θ	R_e	R_p
	$\Omega.cm^2$	Degree	$\Omega.cm^2$	$\Omega.cm^2$
As- abraded	426	35.56	102	234
pH 5.5	478	52.95	47	380
pH 7.5	1409	55.36	103	1280
pH 9.5	210	38.35	44	164

Cyclic voltammetry polarization (CV)

The effect of coating time (5, 10, 20 min) and solution pH (5.5, 7.7, 9.5) on the corrosion behavior of ZE41- Mg alloy samples immersed in corrosive 3.5% NaCl solution was also studied by cyclic voltammetry polarization tests. Concerning the effect of time, the present results revealed that there was an increase in potential (50 mV) in the coated ZE41- Mg alloy for 10 and 20 min compared to as-abraded samples. Moreover, the increase in alloy potential coated for 10 and 20 min was 125 mV when compared with that coated for 5 min (Figure 3). Accordingly, the highest pitting resistance can be obtained from the samples that treated for 10 and 20 min in permanganate coating. However, the samples treated for 10 min, showed a better performance than those treated for 20 min, where the area under the loop was smaller. Moreover, a relative shift towards more passive current was noticed for the samples treated for 10 min compared to that observed at 20 min. The pitting current values were 0.234, 1.621, 0.025 and 0.143 mA/cm² for as-abraded, 5, 10 and 20 min, respectively. Accordingly, the highest protection against pitting corrosion can be sorted as a function of treatment time as in the following order:

10 min > 20 min > as- abraded > 5 min.

This finding was in consistence with EIS and confirmed the important role of treatment time on the permanganate film formed for improving the corrosion resistance of ZE41- Mg alloy.

Regarding the influence of changing the pH of permanganate coating solution on the pitting corrosion of ZE41- Mg alloy, the present results showed that the pitting area under the loop of the coated samples at pH 7.5 was smaller than the other coated samples at pH 5.5 and 9.5 (Figure 4). Surprisingly, the area under the loop of the as-abraded sample was relatively smaller than that obtained from the permanganate coated samples at pH 7.5. This result didn't match with the impedance spectra demonstrated in Figure 1 where the measured surface resistance of permanganate coated samples at pH 7.5 was 1409 Ω.cm² which was about three times the value of as-abraded samples (426 Ω.cm²).
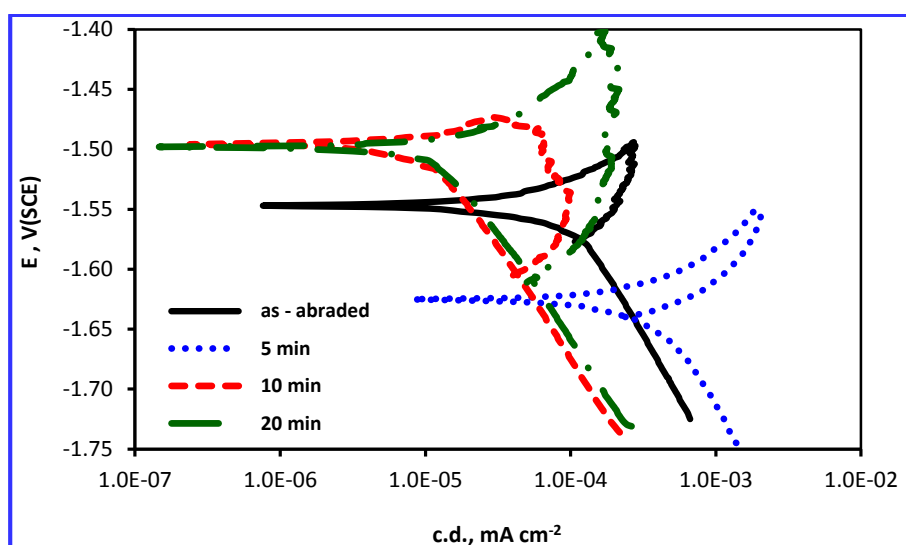
Figure 3: Cyclic voltammetry curves of permanganate coated ZE41– Mg alloy at different treatment times after one week of immersion in 3.5% NaCl solution.

The disagreement between the EIS (Figure 1) and the CV (Figure 4) results could be explained by the fact that the measured surface resistance by EIS expresses the total surface resistance including the pitting, crevice, and general corrosion while CV data represented the pitting corrosion only.
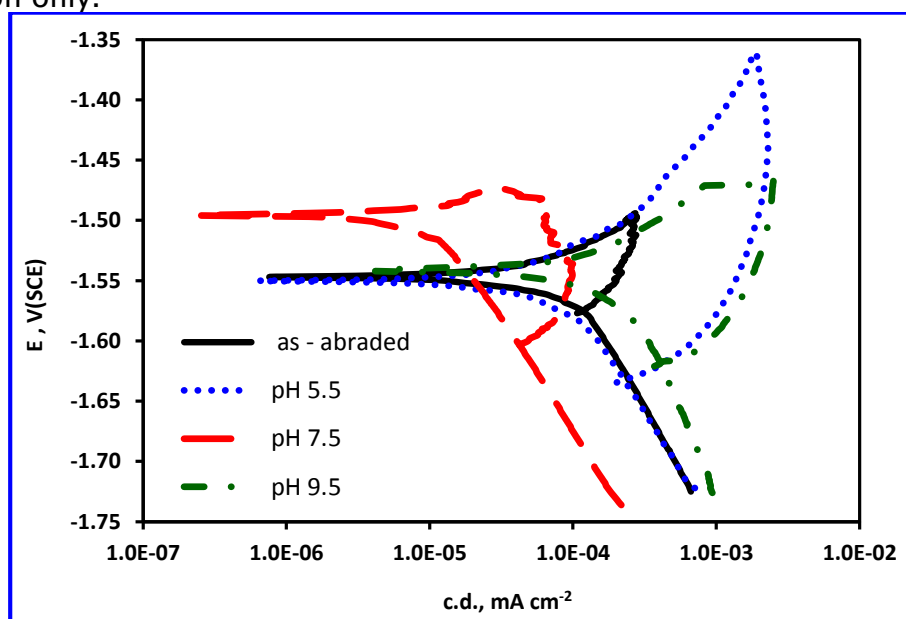

Figure 4: Cyclic voltammetry for as–abraded and permanganate coated ZE41– Mg alloys at different pHs after one week of immersion in 3.5% NaCl solution.

Linear polarization measurements

The stability of the films formed on ZE41– Mg alloys treated in neutral permanganate solutions for different coating times namely 0 (as–abraded), 5, 10, and 20 min, was evaluated in corrosive 3.5% NaCl solution by linear polarization measurements. It is well known that corrosion potential (E_{corr}) and corrosion current density (I_{corr}) are often used to characterize the corrosion protective properties of the oxide layer [20]. In general, it was reported that the high E_{corr} and low I_{corr}, results in a low corrosion rate (C_R) and good polarization resistance (R_p) of the coatings [21]. Figure 5 illustrated that the resultant coatings treated for 10 and 20 min revealed shifts towards more passive E_{corr} when compared with as–abraded samples, while that coated for 5 min shifted towards more negative E_{corr} values. The measured E_{corr} values were –1.7225, –1.7106, –1.6543 and –1.6447 mV while the calculated C_R values were 4.823E–6, 4.732E–6, 4.550E–6 and 3.640E–6 for 5 min, as–abraded (corrosion is done), 10 and 20 min, respectively. Thus, ZE41– Mg alloy treated for 20 and 10 min showed the noblest corrosion potentials and the lowest corrosion rates compared with other samples. Such data confirmed that the best protection can be obtained from the samples that treated for 20 or 10 min according to the following order of passivity:

20 min > 10 min > as–abraded > 5 min

The polarization data seemed to be in a partial disagreement with the EIS and CV measurements. Such disagreement could simply be attributed to the low immersion time (30 min) in corrosive chloride solution used for collecting the polarization data compared with long immersion time (one week) used for all other tests.
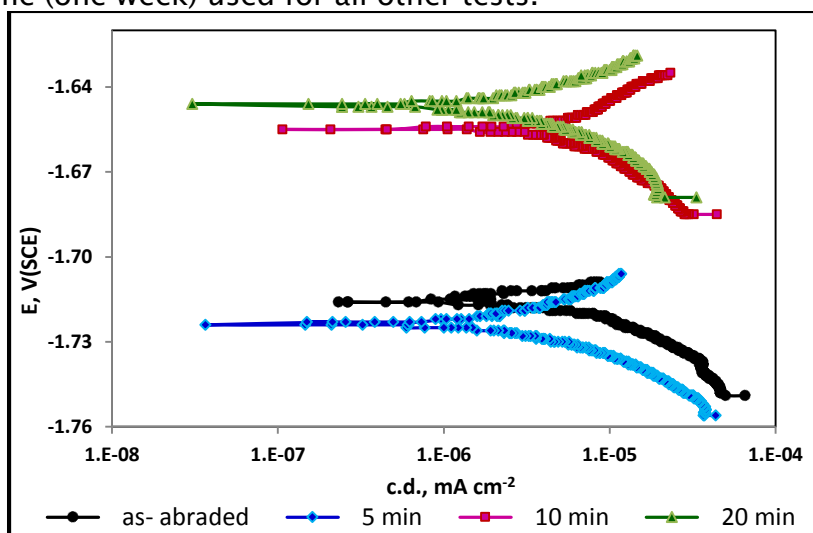

Figure 5: Polarization curves of permanganate coated ZE41– Mg alloy at different treatment times after 30 min of immersion in 3.5% NaCl solution.

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The effect of changing the pH of the coating solution on the corrosion resistance of ZE41–Mg alloys was studied by linear polarization. Figure 6 represented the polarization curves of the as–abraded and the coated ZE41– Mg alloy samples in permanganate solution of different pHs (5.5, 7.5 and 9.5) after corrosion in 3.5% NaCl solution. The polarization parameters of as–abraded and coated samples at different pHs were tabulated in Table 2. Figure 6 and Table 2 illustrated that, the polarization curve of the as–abraded sample showed increasing current in the anodic part due to aggressive attack of chloride ions and dissolution of the alloy had happened until it reached a passive behavior that presented due to the formation of oxide layer on the alloy surface with low anodic current densities [22]. The dissolution of the as–abraded magnesium alloy in neutral NaCl solution might be due to the transformation of $Mg(OH)_2$ to easily soluble $MgCl_2$ [23, 24].

Although in the coating solution of pH 9.5 the ZE41– Mg alloy had the noblest E_{corr} value; it had the highest I_{corr} and C_R values which agreed with EIS measurements. The permanganate coated samples at pH 7.5 showed the lowest I_{corr}, C_R and the highest R_p values. In addition, the limiting current (I_l) of the ZE41– Mg alloy coated with permanganate at pH 7.5 showed a horizontal shift towards the negative (more passive) direction compared with the other samples. The lowest corrosion current density obtained in the case of permanganate coating of pH 7.5 may be due to the presence of thin and compact layer of the coat resist the aggressive attack of chloride ions [22]. According to R_p values in Table 2, the order of passivity will be:

pH 7.5 > pH 9.5 > as–abraded > pH 5.5

This order was somewhat different from that observed by EIS measurements. This disagreement in results might be attributed to the low immersion time used for collecting the polarization data (30 min) compared with long immersion time (one week) used for all other tests. These results provided evidence that coating of ZE41– Mg alloy with permanganate solution of pH 7.5 offered the best corrosion resistance.
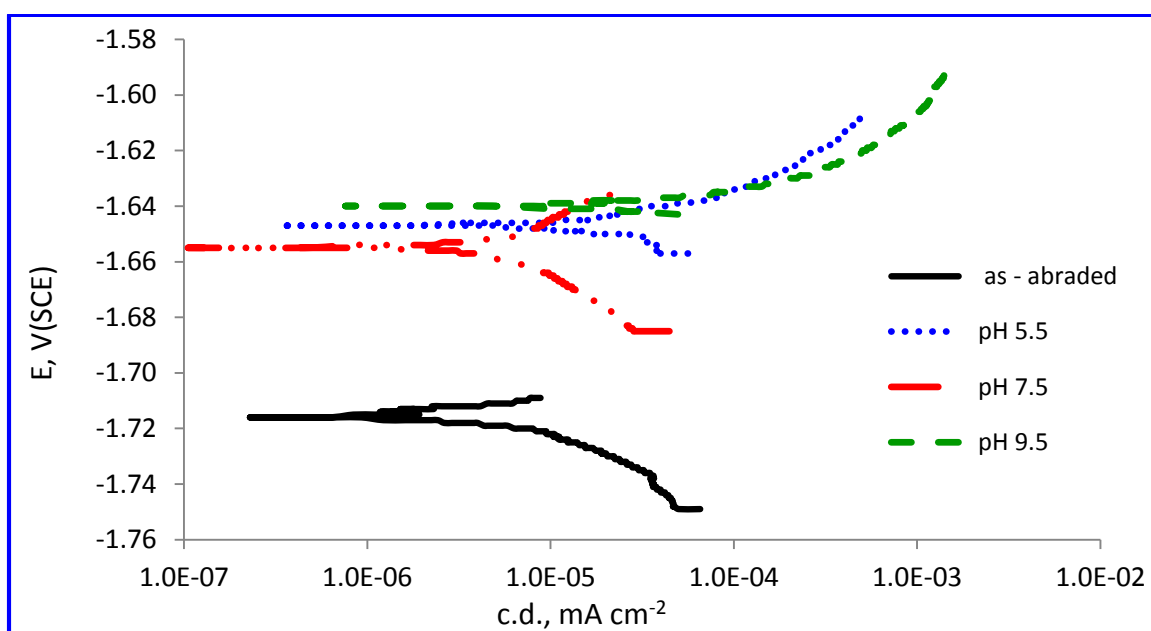
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Figure 6: Linear polarization for as–abraded and permanganate coated ZE41– Mg samples at different pHs after 30 min of immersion in 3.5% NaCl solution.

Table 2: Polarization data for as–abraded and permanganate coated magnesium alloy samples at different pHs after 30 min of immersion in 3.5% NaCl solution

Media	E_{corr}	$I_{corr} \times 10^{-6}$	$I_l \times 10^{-6}$	$C_R \times 10^{-6}$	R_p
	mV	Acm^{-2}	Acm^{-2}	mpy	$\Omega.cm^2$
As–abraded	−1.7106	5.2	0.65	4.732	14.98
pH 5.5	−1.6483	25.0	2.00	22.75	11.81
pH 7.5	−1.6543	5.0	0.55	4.550	92.27
pH 9.5	−1.6400	31.0	6.00	28.21	44.02

Surface examination
Visual inspection and macro-images

Figure 7 represents the macro–image of as–abraded and coated ZE41– Mg samples at different coating times after immersion for a week in 3.5% NaCl solution. The image showed severe attack for as–abraded sample due to different localized corrosion forms as galvanic, pitting and crevice upon immersion in corrosive solution. On the other hand, samples coated for 10 min showed a marked resistance against localized corrosion compared with the other ones. Obviously, the film formed due to permanganate coating for 10 min played a vital role by acting as a barrier to prevent the chloride attack where the number of pitting zones and

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crevice areas reduced significantly. The pitting density decreased from 30% for the as-abraded sample to be 5% after permanganate coating for 10 min. Crevice corrosion was also decreased and observed in just few areas after 10 min permanganate treatment. Figure 7 also revealed a sharp increase in localized corrosion for the samples that treated for 20 min but still less than the dramatic deterioration that happened for the samples treated for 5 min where the pitting densities were 50% and 10% for coating times 5 and 20 min, respectively. Accordingly, permanganate treatment for 10 min is the best condition for corrosion protection of ZE41-Mg alloy.
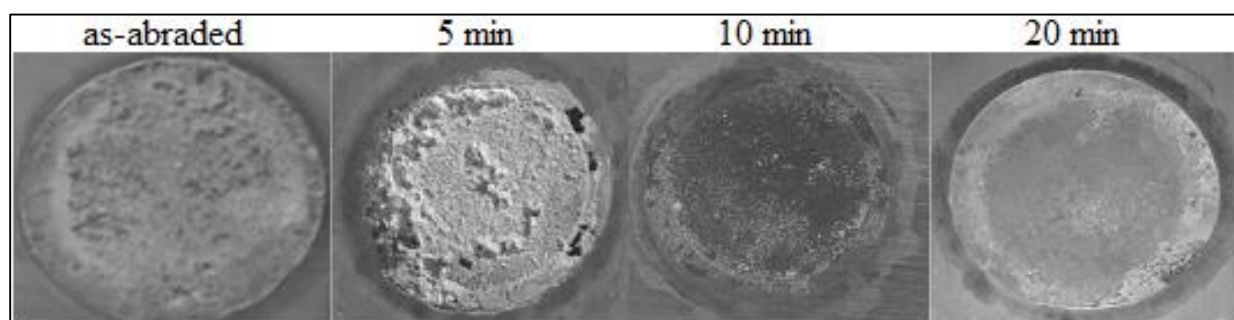
Figure 7: Macroscopic images for surface resistance of as-abraded and coated ZE41- Mg alloy samples at different coating times after immersion for a week in 3.5% NaCl solution.

Figure 8 demonstrated the effect of changing the pH of permanganate coating solution on the corrosion resistance of ZE41- Mg alloy. After one week of immersion in corrosive NaCl solution, the samples coated with permanganate at pH 5.5 and 9.5 showed severe pitting and crevice corrosion close to the behavior of as-abraded sample. Conversely, the samples coated with permanganate at pH 7.5 showed the best corrosion protection. Only few tiny pits with limited areas of crevice corrosion were observed.

The average pitting density after one week of immersion in 3.5% NaCl solution is 30, 20, 5 and 50% for as-abraded, pH 5.5, pH 7.5 and pH 9.5, respectively. Results showed that the high pitting susceptibility can be sorted in the following order:

pH 9.5 > as-abraded > pH 5.5 > pH 7.5

Accordingly, the film formed due to permanganate coating at pH 7.5 was the best to offer acceptable localized corrosion resistance to Mg substrate. Changing the neutral pH of permanganate coating (pH 7.5) towards acidic (pH 5.5) or alkaline (pH 9.5) enhanced the formation of less protective films. Decreasing the passivity due to changing the pHs either towards acidic or alkaline values could be attributed to the changes in the chemical composition of the films formed.
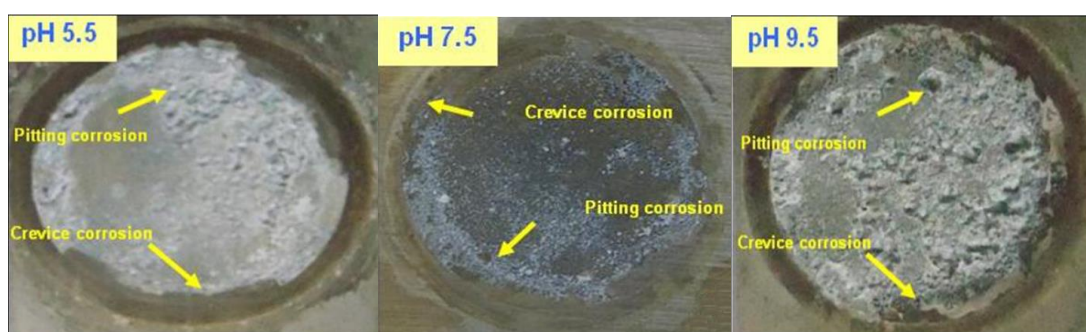
Figure 8: Macroscopic images for the effect of changing the permanganate coating pH on the corrosion resistance of ZE41- Mg alloy after one week of immersion in 3.5 % NaCl solution.

X-ray diffractometry (XRD)

The chemical composition of the film formed due to permanganate treatment was performed using X-ray diffractometry. Figure 9 illustrated the effect of changing the coating time on the corrosion products formed on ZE41- Mg alloys after one week of immersion in 3.5% NaCl solution. All samples showed similar chemical composition of Mg and $Mg(OH)_2$ except the samples that treated for 10 min where most of the peaks identified were for Mg without $Mg(OH)_2$. The chemistry behind such behavior is unclear.

The effect of changing the pH of the coating solution from neutral to acidic and alkaline (at 10 min coating time) on the composition of the film formed over the surfaces of ZE41- Mg alloys was illustrated in Figure 10. The results demonstrated that XRD spectra of the corrosion products formed at pH 7.5 revealed presence of Mg as a metal while other coated samples at pH 5.5 or 9.5 revealed formation of both Mg and $Mg(OH)_2$.

After permanganate treatment, it was expected that a film rich with Mn would be formed on the magnesium alloys surfaces. The observed film formed at pH 7.5 had a dark brown color which according to Pourbaix diagram [25] suggested being Mn_2O_3. Manganese trioxide is a strong oxidizing agent and thermodynamically more stable than the other films formed at different pH conditions under investigation. Generally, XRD was not able to detect the presence of Mn in all films formed at different pHs or at different coating times. This finding indicated that such films were relatively thin and out of the accuracy limits of XRD instrument.
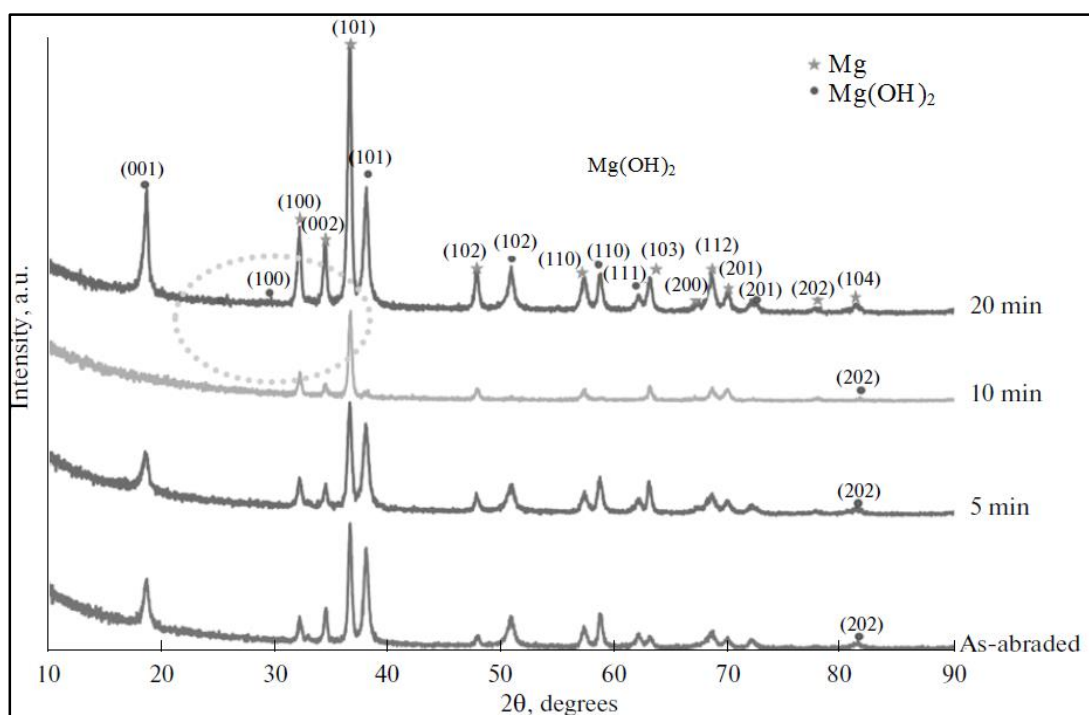
Figure 9: XRD analysis of the corrosion products formed at the as-abraded and permanganate coated samples at different coating times after one week of immersion in 3.5% NaCl solution.
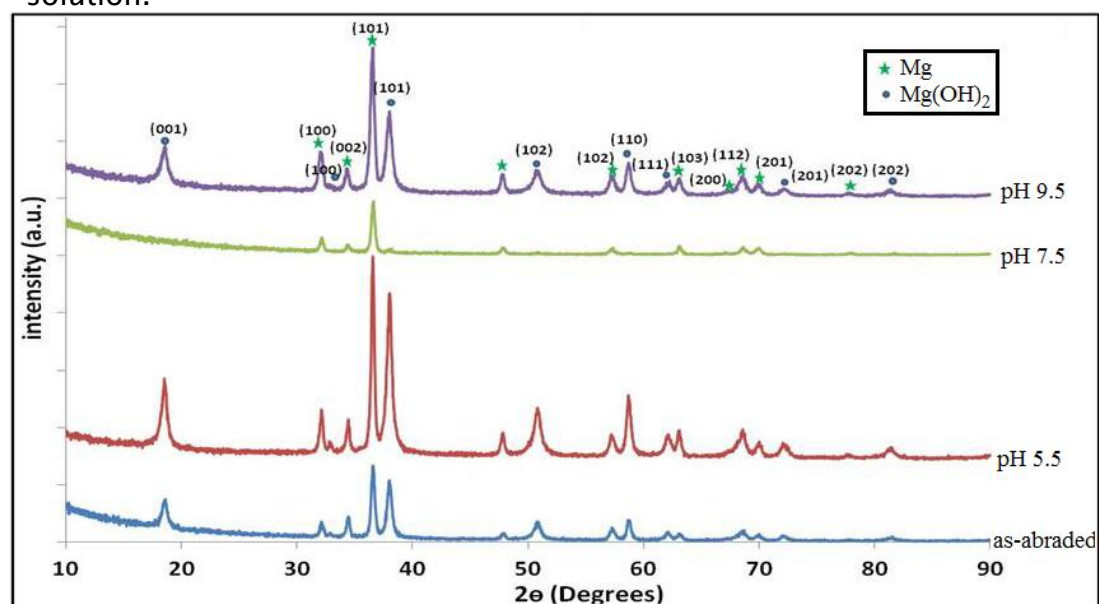

Figure 10: XRD analysis of the corrosion products formed over permanganate coated samples at different pHs after immersion in 3.5% NaCl solution compared with as-abraded samples.

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It is worth to mention that an XRD spectrum of the sample treated at 10 min (Figure 9) was the same of that treated at pH 7.5 (Figure 10). Under these conditions of time and pH, the samples showed a unique chemical composition compared with other samples. However, it would be suggest that the stable protective Mn_2O_3 film formed at pH 7.5 for 10 min coating time might have a catalytic effect to inhibit the formation of $Mg(OH)_2$. The formation of such film might be the reason behind the presence of only Mg metal in case of the samples that treated at pH 7.5 for 10 min and formation of magnesium hydroxide, $Mg(OH)_2$, in the other samples.

SEM-EDX micrographs

SEM micrograph and EDX microprobe analysis of the as-abraded magnesium alloy before corrosion in 3.5% NaCl solution revealed occurrence of rare-earth (Gd and Nd) and zinc which presented as alloying elements in ZE41-Mg substrates (Figure 11 a, b).

However, the surface distribution of these elements presented on the Mg alloy substrate was not uniform and hence, some surface defects which stimulated pitting corrosion on ZE41-Mg alloy upon immersion in NaCl solution were observed [26]. Moreover, the sharp potential difference among the rare-earth elements phases (cathode) inside the Mg matrix (anode) resulted in building up micro-electrochemical cells and enhancing galvanic corrosion [27, 28]. Upon immersion in corrosive chloride solution, the galvanic corrosion propagated and enhanced intergranular corrosion around the rare-earth phases. At the end, the rare-earth phases could separate from the matrix and left holes. These holes could make a big confusion under the microscopic examination because they appeared like pitting corrosion (Figure 11-c). The EDX of the uncoated sample after one week of immersion in 3.5% NaCl solution (Figure 11-d) indicated the disappearance of the rear earth elements and presence of oxygen and chloride elements which came to the surface from salt water. The appearance of calcium might be due to the presence of impurities in salt solution.

SEM images of Figure 12 illustrated the effect of coating time on the surface morphology of the ZE41- Mg alloy. Microstructure examination of the film formed due to permanganate treatment for 10 min revealed a uniform, dense and compact surface morphology with limited areas of defects. Conversely, magnesium alloy samples that subjected to permanganate treatment for 5 or 20 min revealed large areas of coatings defects. The presence of such defects reduced the coating efficiency and decreased its barrier properties. This provided an explanation for the improvement in the localized corrosion resistance of the samples that treated in permanganate solution for 10 min compared with the other conditions.
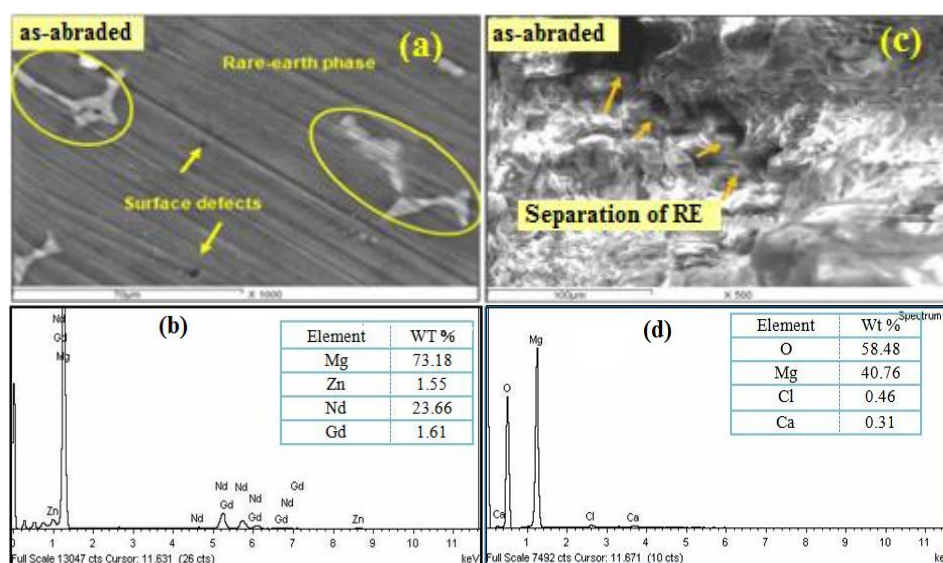
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Figure 11: SEM-EDX for the uncoated (as-abraded) samples before (a, b) and after (c, d) one week of corrosion in 3.5 % NaCl solution.
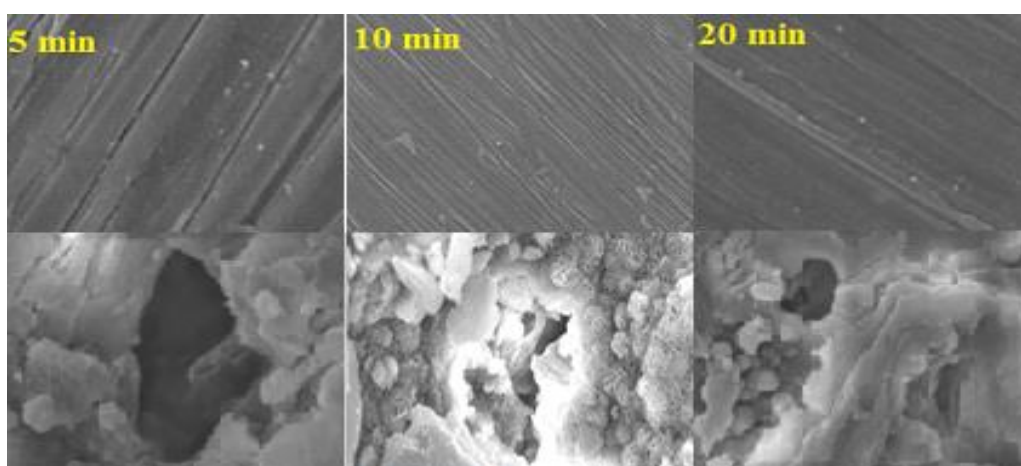

Figure 12: SEM micrograph for the permanganate coated samples at different coating times (upper) before corrosion and (lower) after one week of immersion in 3.5 % NaCl solution.

Concerning the effect of pH of the permanganate coating solution on samples surface morphology, it was observed that samples that coated at pH 7.5 showed a distinct reduction in the number and the size of pits and holes compared with those coated at solution of pHs 5.5 or 9.5 (Figure 13). This ensured that neutral pH is the best medium for permanganate coating solution.

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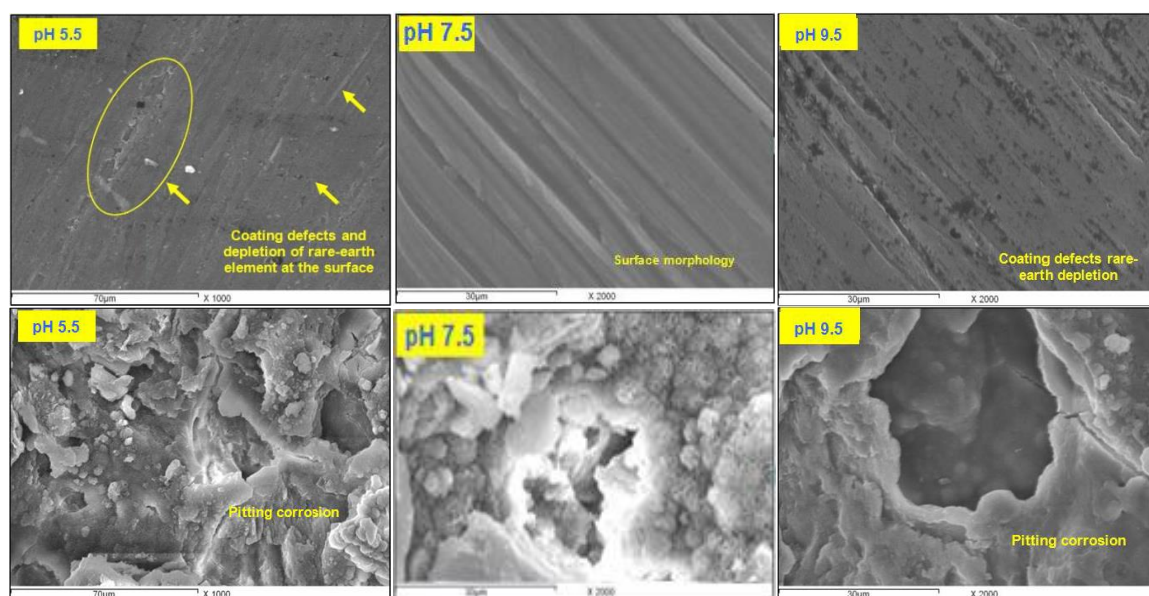
Figure 13: SEM micrograph for the permanganate coated samples at different pHs before (upper) corrosion and after (lower) one week of immersion in 3.5 % NaCl solution.
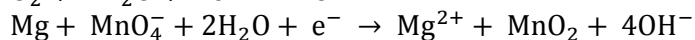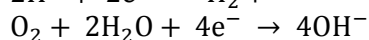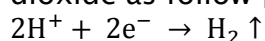
Mechanism of coating formation

It is well known that Mg is very active in salt water and undergoes anodic dissolution as follow [22, 28]:

$$Mg \rightarrow Mg^{2+} + 2e^-$$
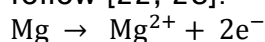
The alloying elements also get dissolved in the corrosive medium and thus the anodic reactions occur as follow:

$$Zn \rightarrow Zn^{2+} + 2e^-$$
$$Nd \rightarrow Nd^{3+} + 3e^-$$
$$Gd \rightarrow Gd^{3+} + 3e^-$$
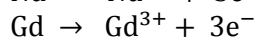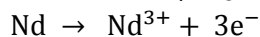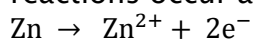
The main cathodic reaction is the hydrogen ion reduction and also the reduction of dissolved oxygen in addition to the reduction of permanganate ions to produce manganese dioxide as follow [5, 12]:

$$2H^+ + 2e^- \rightarrow H_2 \uparrow$$
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
$$Mg + MnO_4^- + 2H_2O + e^- \rightarrow Mg^{2+} + MnO_2 + 4OH^-$$

Thus, the local pH values in cathodic sites increased and the metals hydroxides can be formed [5].
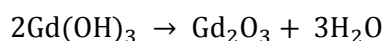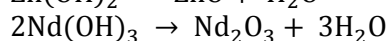
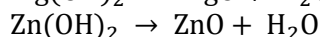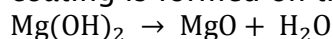$$M^{n+} + nOH^- \rightarrow M(OH)_n$$
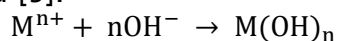
Where, n is the oxidation state of the metal (M) which may be the base Mg or any alloying element in the structure of the alloy.

The produced MnO_2 will undergo successive reduction reactions to lower oxides to form a surface layer in which a various oxides coexist [13].

$$2MnO_2 + 2H^+ + 2e^- \rightarrow Mn_2O_3 + 2H_2O$$
$$3Mn_2O_3 + 2H^+ + 2e^- \rightarrow 2Mn_3O_4 + H_2O$$
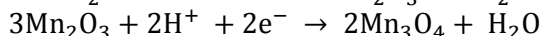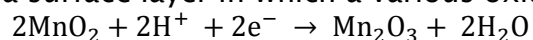
Therefore, oxides of manganese in addition to hydroxides of Mg, Zn and rare earth elements deposit on the surface of the alloy. Finally, the hydroxides dehydrate and conversion coating is formed on the alloy surface [5].

$$Mg(OH)_2 \rightarrow MgO + H_2O$$
$$Zn(OH)_2 \rightarrow ZnO + H_2O$$
$$2Nd(OH)_3 \rightarrow Nd_2O_3 + 3H_2O$$
$$2Gd(OH)_3 \rightarrow Gd_2O_3 + 3H_2O$$

According to XRD analysis, metal oxide can be formed via the formation of metal hydroxide and its subsequent dehydration. This was happened at coating solution of pH 5.5 and 9.5 at coating time 5 and 20 min. While at coating solution of pH 7.5 and at 10 min coating time, the metal oxide can be formed according to direct oxidation as in the following equation:

$$2Mg + O_2 \rightarrow 2MgO$$
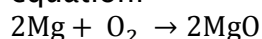
CONCLUSIONS

1- Alloying magnesium with rare earth elements enhanced the galvanic corrosion and decreased the overall corrosion resistance of the alloys.

2- The obtained results allowed conditions to be established for optimization the permanganate treatment time to be 10 min and pH to be 7.5 to obtain a maximum protection for ZE41- Mg alloy in corrosive chloride solutions.

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

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