



# Corrosion Behavior of Chromium Conversion Coated AZ91C Magnesium Alloy in Sodium Borate and Sodium Chloride Aqueous solutions

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**Abstract**— A chromium containing film was deposited on the surface of the investigated AZ91C magnesium alloy by chemical conversion process. The microstructure and surface morphology of the as- received and coated alloys were initially characterized by optical microscope. The corrosion behavior of AZ91C before and after coating was studied through weight loss technique by immersion in 3.5% NaCl and borate solutions at various concentrations and pH values. Surface corrosion products and passivation films were analyzed by X-ray diffraction. The obtained results showed that AZ91C coated with chromium conversion coating exhibits enhanced corrosion resistance, furthermore X-ray diffraction revealed that corrosion damage was mainly caused by formation of crystalline phase  $Mg(OH)_2$ . The addition of borate with different concentration enhanced the protection with efficiency of 86% recorded at 0.2N sodium borate concentration and 3.5% NaCl.

**Index Terms:** Corrosion behavior, AZ91C alloy, chromate conversion coating, NaCl.

## I. INTRODUCTION

Magnesium and magnesium alloys are widely used in various engineering applications especially as structural materials because of their good mechanical and physical properties [1, 2]. Properties such as ultralightness, high strength to weight ratio, excellent cast ability, high damping capacity, as well as a low density (about two thirds of aluminum and one fourth of iron) increased the presence of magnesium and its alloys in aerospace, automotive, and electro-communication fields [3-5]. For engineering applications, Mg is usually alloyed with one or more elements, which include aluminum (Al), manganese (Mn), rare earth (RE) metals, lithium, zinc (Zn), and zirconium (Zr) [6]. Magnesium alloys are identified and standardized worldwide by the ASTM

standards where alloys are marked with letters indicating the main alloying elements, followed by figures of each element in weight percentage, and the last letter in every identification number means the stage of development of the alloy (A, B, C, etc.). The alloy AZ91C, for example, is an alloy with a rated content of 9% aluminum (A) and 1% zinc (Z). Its development stage is 3 (C). ASTM specifies the following composition for the above designation C (all values wt%): Al 8.3–9.7; Zn 0.35–1.0; Si (max.) 0.10; Mn (max.) 0.15; Cu (max.) 0.30; Fe (max.) 0.005; Ni (max.) 0.002; others (max.) 0.02. The AZ alloys, which contain Zn as a secondary alloying element, solidify with a sufficiently fine grain size to meet most property requirements. They are highly castable and have a minimum tendency toward hot cracking; this tendency increases with increasing Zn content. These alloys also, however, have a tendency to develop micro-porosity. The magnesium- aluminum system has been the basis of the most widely used magnesium casting alloys since these materials were introduced in Germany during the First World War [7]. Most of these alloys contain 8-9% aluminum with small amounts of zinc. Among these types the AZ91 series alloys have found widespread applications in the automotive industry due to its relatively low cost and generally adequate mechanical properties and processing characteristics [8].

The unwise use of magnesium in wet environments gives rise to its poor corrosion reputation [9]. Magnesium has poor corrosion resistance due to its standard potential ( $E^\circ = -2.363$  V/SHE (standard hydrogen electrode)), therefore it is extremely susceptible to galvanic corrosion [10]. The poor corrosion resistance of magnesium and its alloys lies on two aspects including: the oxide films forming on the surface are not perfect and nor protective, and galvanic corrosion can be caused by impurities, secondary phases such as  $Mg_{17}Al_{12}$ ,  $AlMn$ ,  $Al_8Mn_5$ ,  $Mg_{12}Nd$ , and  $Mg_2Pb$ , even when connected with notably iron, nickel and copper [11]. A serious limitation for the potential use of several magnesium alloys, and AZ91 in particular, is their susceptibility to corrosion. Magnesium

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alloys, especially those with high purity, have good resistance to atmospheric corrosion. However, the susceptibility to corrosion in chloride containing environments is a serious concern [12].

In order to decrease their corrosion sensitivity, several processes can be used to deposit a protective film on the surface of the alloy: anodizing, sol-gel process, gas-phase deposition process and chemical conversion, the least expensive and the easiest to perform among these methods is the chromate chemical conversion coating [4]. Major reasons for the widespread use of chromating are the self-healing nature of the coating, the ease of application, the high electric conductivity and the high efficiency: cost ratio. These advantages have made them a standard method of corrosion protection [13]. The coating is formed by reaction between ions in the deposition bath and metal cations dispersed to the bath during the initial corrosion reaction between the bath and coated metal [14, 15]

One of the barriers limiting wide applications of magnesium alloys to various industries is their poor corrosion resistance. The corrosion properties of AZ91 magnesium alloy, which is the most popular magnesium casting alloy, are affected by microstructural and environmental factors. The corrosion properties of AZ91 magnesium alloy are affected by the corrosion properties of alpha-Mg and beta phases, the volume fraction and distribution of beta phase and area ratio of alpha-Mg/beta phases. The corrosion properties of AZ91 magnesium alloy under various environments also change according to the passivity of films and types of corrosion products formed on its surface. The corrosion resistance of the magnesium alloys can be improved by microstructural control through the addition of alloying elements and optimization of the production process [16]. The aim of this work is to study the corrosion behavior of magnesium alloys AZ91C in salt and borate solutions at different concentration. The corrosion protection after treatment with chromium conversion coating was evaluated.

## II. MATERIALS AND METHODE

### A. Materials

Specimens with thickness of 7 mm were taken from the AZ91C die-cast material available in cylindrical rod with a diameter of 50 mm. The chemical composition of the alloy is given in Table1. For ease handling, the specimens were encapsulated in epoxy resin.

TABLE 1. Chemical composition of the used alloy

Element	Al	Zn	Mn	Si	Cu	Fe	Be	Mg
W %	8.03	0.53	0.18	0.064	0.035	0.012	0.0004	BAL.

### B. Corrosive media

The testing environments for corrosion immersion tests were: (a) 3.5% NaCl (pH = 1, 2, 6, 7 and 9); (b) 3.5% NaCl with Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> buffer solution of different concentrations (0.05 N, 0.1 N, 0.15 N, and 0.2% N); (c) Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> Buffer solution of different concentrations (0.05N, 0.1N, 0.15N and 0.2N).

### C. Immersion testing

Corrosion resistance of material is measured by weight loss method (immersion test) of the immersed samples in above mentioned environments for 24 hours following ASTM standard procedures [17, 18], samples were cleaned, degreased, and corrosion products on the samples surfaces were removed and weighted on an analytical balance (measuring accuracy  $\pm 0.0001$  g). The test was repeated for the coated samples following the standard testing procedure [19]. For the immersion tests, the specimens were encapsulated in epoxy resin with an exposed surface.

### D. Surface morphology and corrosion product analysis

The surface morphology and corrosion product analysis of the treated and untreated specimens were characterized using the optical microscope, and X-ray diffraction (XRD) using X-ray diffractometer (Panalytical X'pert Pro) with radiation of Cu K $\alpha$ 1 ( $\lambda = 1.5406$  Å).

### E. Chromate conversion coating experiments

Samples were prepared by the preparation procedure illustrated in figure1 and then chemical conversion experiments were done in bath has composition given in table 2.

TABLE 2. The chemical conversion coating bath

Composition	Quantity	Operating condition
Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	180 g	The samples were treated at room temperature for 90s and exposed to the atmosphere for 5s before being washed and drained
HNO <sub>3</sub> 60%	261 ml/L	

## III. RESULTS AND DISCUSSIONS

### A. Immersion testing of AZ91C in salt water before chromate coating

Corrosion rates in various environments were determined as the rate of weight loss per unit surface area and presented in figures 2. The figure shows the effect of pH on the corrosion rate of the investigated alloy. The lowest corrosion rate was recorded at pH 1 (56 mpy) followed by pH 7 while the maximum corrosion rate was at pH 6 (388 mpy). The morphology of the tested specimens is shown in figure 3. These photos show that specimen tested at pH 6 suffers from severe corrosion in the form of large pit on its surface. Specimen tested at pH 9 suffers from corrosion also. On the other hand specimens tested at pH 1 do not show a noticeable corrosion.

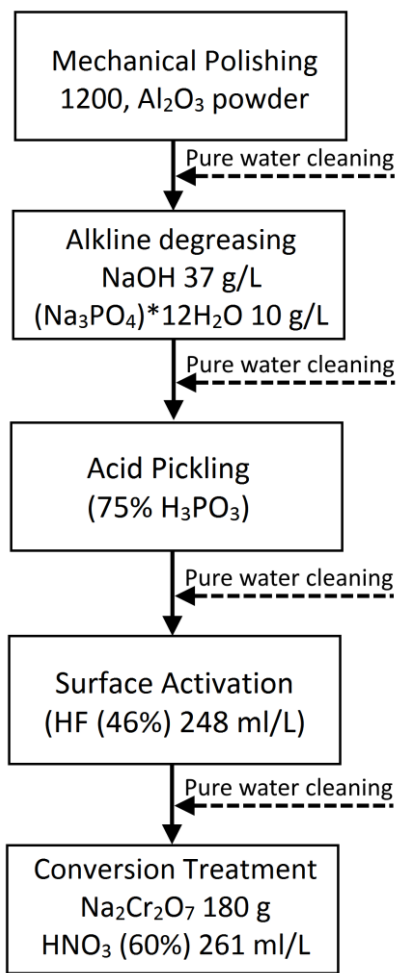


Figure 1. Outline of the procedure for the substrate surface preparation and chemical treatment

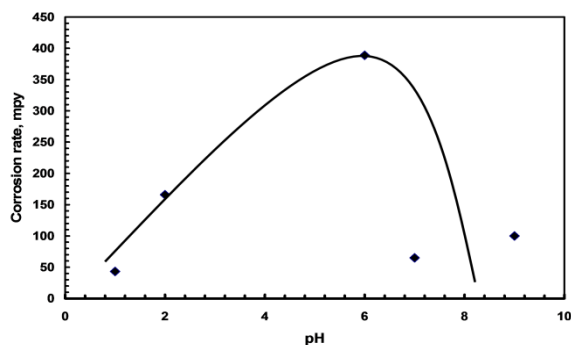


Figure 2. Effect of pH on the corrosion rate of AZ91C alloy

**B. Immersion testing of AZ91C in sodium borate before chromate coating**

Sodium borate (Borax) is the sodium tetraboratedecahydrate ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) that, when dissolved in water, is hydrolyzed to boric acid and  $\text{OH}^-$  anions, yielding a pH of about 9.13 [20], and it is anodic inhibitor forms protective films that decrease the cathodic reactions rate by blocking the oxygen chemisorption and or limiting the diffusion of oxygen to the metal surface in near-neutral and alkaline solutions [21].

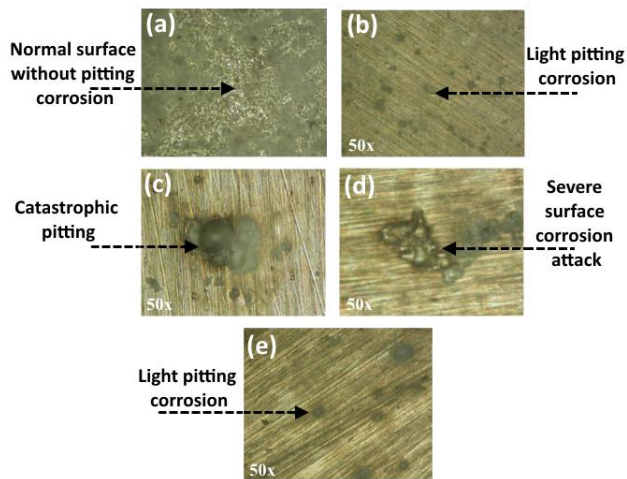


Figure 3. Optical micrographs for the corroded samples after immersion test in 3.5% NaCl at (a) pH =1, (b) pH =2, (c) pH =6, (d) pH =7, and (e) pH =9

The addition of  $\text{Na}_2\text{B}_4\text{O}_7$  to 3.5% NaCl solution exerts a pronounced corrosion inhibition. The highest inhibition is shown by the lowest concentration of Borate (0.05 N). Increasing borate concentration leads to decreasing inhibition or increasing corrosion rate as shown in Figure 4. The optical micrographs of the tested specimens are shown in Figure 5. Again these micrographs ascertain what was obtained by the weight loss measurements. Figure (5a) shows that the specimen suffers from slight uniform attack while Figures (5b, c, and d) show severe attack with corrosion products on the surface of specimens.

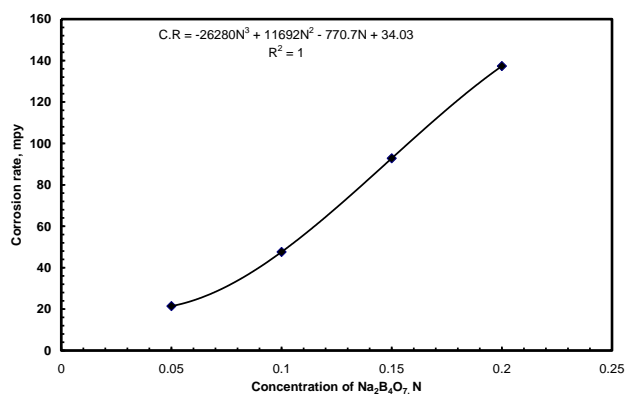


Figure 4. The effect of addition of  $\text{Na}_2\text{B}_4\text{O}_7$  to 3.5% NaCl

**C. Immersion testing of AZ91C in sodium borate**

The results of weight loss measurements in presence of only sodium borate are shown in Figure 6. In general low corrosion rates were obtained at all concentrations. Again 0.05N concentration gives the lowest corrosion rate (8 mpy). Other concentration give higher corrosion rates (25-35 mpy). Optical micrographs of the tested specimens are shown in Figure 7. As shown by Figure 7a, specimen tested at 0.05N borate does not show any corrosion. On the other hand, other specimens suffer from corrosion attack as evidenced by the corrosion products formed on the specimen surface.

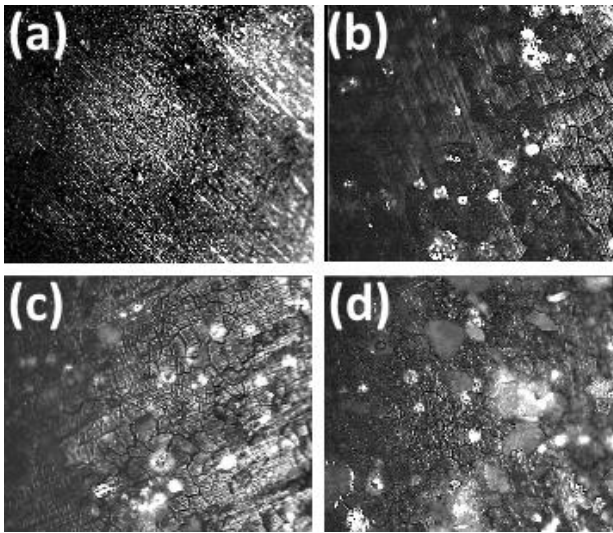


Figure 5. Optical micrographs (200X) for the corroded samples after addition of  $\text{Na}_2\text{B}_4\text{O}_7$  to 3.5% NaCl: the concentration of  $\text{Na}_2\text{B}_4\text{O}_7$  was: (a) Conc.=0.05 N, (b) Conc.=0.1 N, (c) Conc.=0.15 N, and (d) Conc.=0.2 N

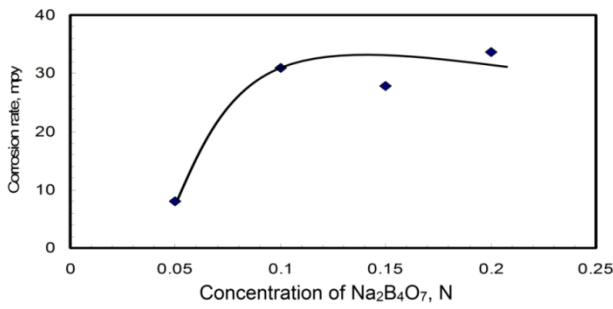


Figure 6. Effect of addition of  $\text{Na}_2\text{B}_4\text{O}_7$  only on corrosion rate of investigated alloy

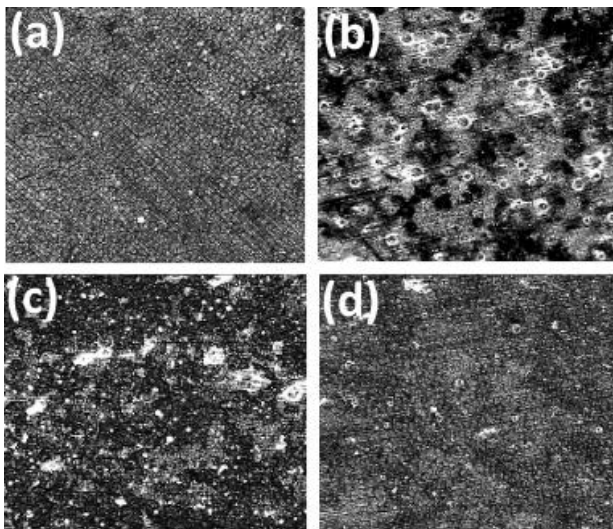


Figure 7. Optical micrographs (200X) for the corroded samples in  $\text{Na}_2\text{B}_4\text{O}_7$ : the concentration of  $\text{Na}_2\text{B}_4\text{O}_7$  was: (a) Conc.=0.05N, (b) Conc.=0.1N, (c) Conc.=0.15N, and (d) Conc.=0.2N

**D. Immersion testing of AZ91C in salt water after chromate coating:**

Surface treatment of the investigated alloy results in a large decrease in corrosion rate. Values as low as (~11mpy) were obtained for the specimen tested at pH = 7, 9 as shown in Figure. 8. The optical micrographs of the

surface treated specimens are shown in Figure 9. Flaky surface layer was obtained, however, this layer seems to be more compact and homogeneous on specimen tested at pH = 2.

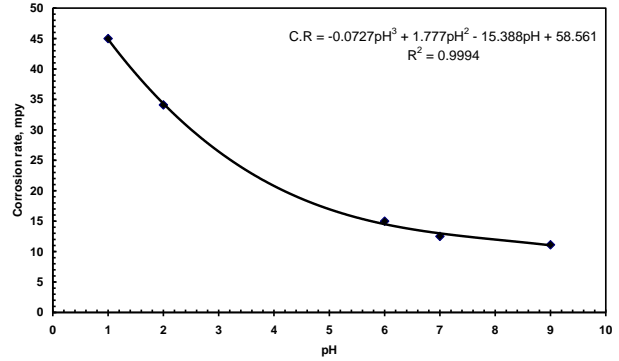


Figure 8. Effect of conversion coating on corrosion rate in 3.5% NaCl

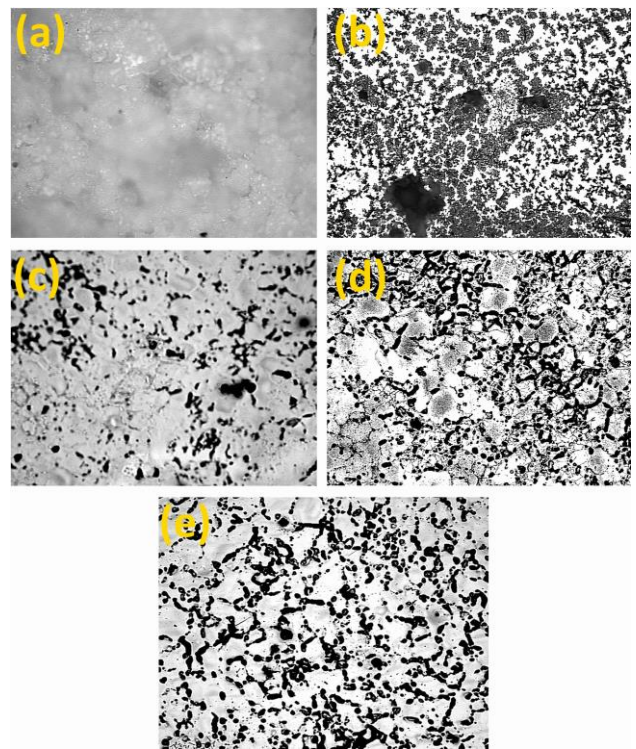


Figure 9. Optical micrographs (200X) show the surface morphology of corroded samples in 3.5% NaCl solution after conversion coating, (a) pH=1, (b) pH=2, (c) pH=6, (d) pH=7, and (e) pH=9

**E. Immersion testing of treated AZ91C in sodium borate**

The addition of sodium borate with different concentrations to the surface treated specimens exerts effect on the corrosion rate of tested specimens as shown in Figure 10. However, the optical micrographs presented in Figure 11 show that the morphology of corroded samples in 3.5% NaCl and  $\text{Na}_2\text{B}_4\text{O}_7$  after conversion coating at different concentrations are more homogeneous and complete coverage to the surface.

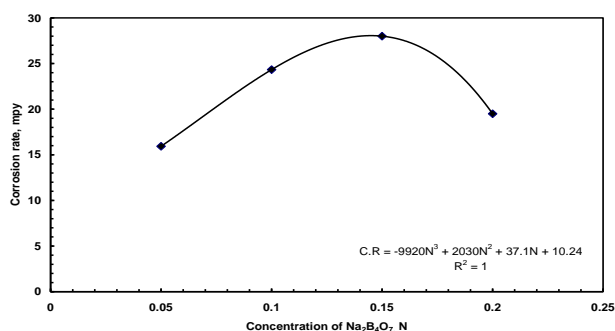


Figure 10. The effect of addition Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> to 3.5% NaCl after conversion coating

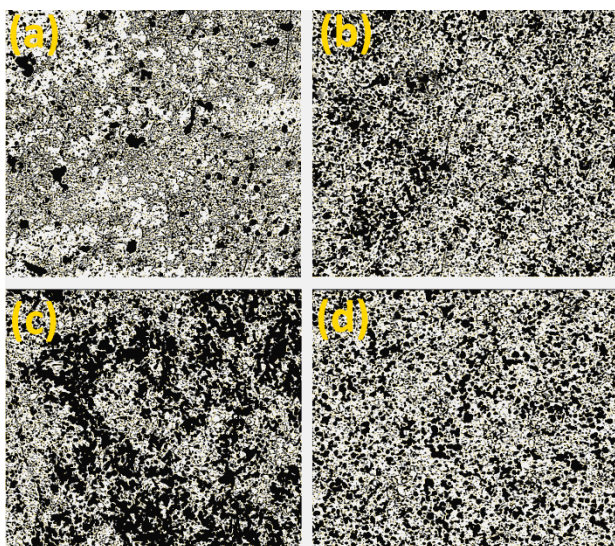


Figure 11. Optical micrographs (200X) show the morphology of corroded samples in 3.5% NaCl and Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> after conversion coating: (a) Conc.=0.05N, (b) Conc.=0.1N, (c) Conc.=0.15N, and (d) Conc.=0.2N

F. Protection Efficiencies

The protection efficiency is calculated as per following formula:

$$\text{Protection Efficiency (\%)} = 100 * (\text{CR}_{\text{unprotected}} - \text{CR}_{\text{protected}}) / \text{CR}_{\text{unprotected}}$$

where:

**CR<sub>unprotected</sub>** = Corrosion rate without surface treatment/before addition of inhibitor

**CR<sub>protected</sub>** = Corrosion rate with surface treatment/addition of inhibitor

Table 3 shows the efficiency enhancement after immersing surface treated samples in 3.5% NaCl with variable pH values, where highest efficiency value recorded with pH of 6, in which maximum weight loss took place before surface treatment.

Table 2. Effect of variable of 3.5% pH values on enhancement corrosion efficiency

pH	1	2	6	7	9
Efficiency (ζ) %	19.6	79	96	81	84

Table 4 represents improved efficiencies after immersed surface treated samples in 3.5%

NaCl+Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> with different concentrations, the highest value recorded at concentration of 0.2N

Table 4. Effect of adding Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> to NaCl on corrosion efficiencies

Concentration (N)	0.05	0.1	0.15	0.2
Efficiency (ζ) %	26	49	70	86

Table 5 represents the efficiency enhancement during immersion of surface treated samples in sodium borate solution only with different concentrations, the highest value recorded at concentration of 0.1N.

Table 5. Effect of sodium borax concentration on corrosion efficiency of AZ91C Mg alloy

Concentration (N)	0.05	0.1	0.15	0.2
Efficiency (ζ) %	71	72	50	62

G. XRD analysis

XRD analysis of surface treated by chromate coating

Figure 12 shows the XRD spectra of coated AZ91C-Mg alloy substrate of selected bath deposited by conversion coating. The peak intensity is observed to be high for chromium oxide that indicates a better crystallinity and the formation of more crystallites with well-defined orientation

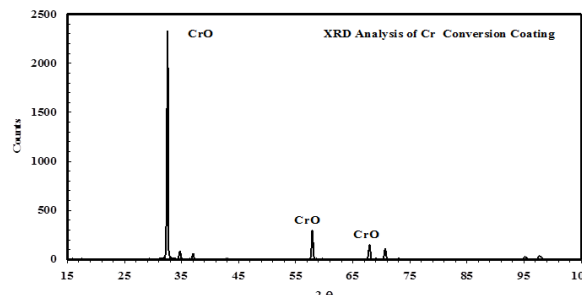
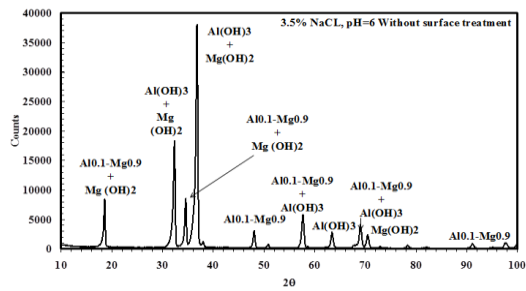


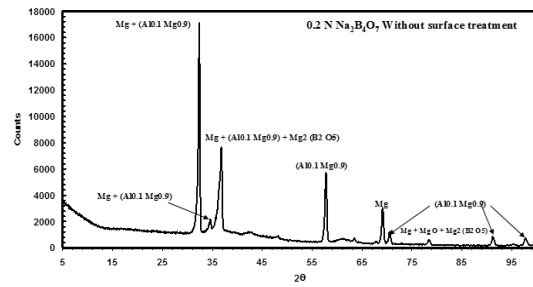
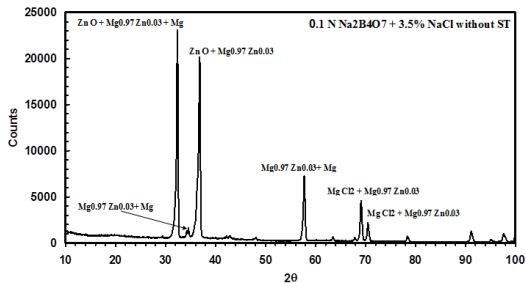
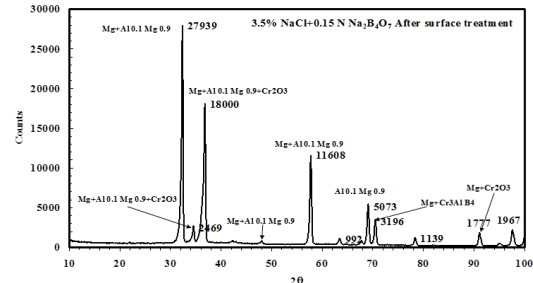
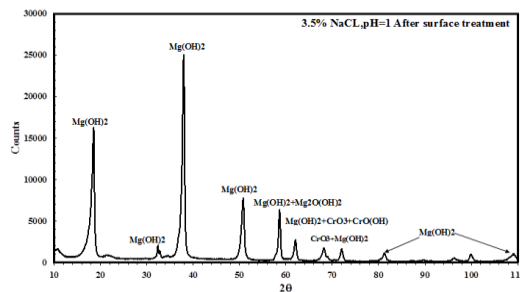
Figure 12. XRD pattern of CrO alloy growth on AZ91C substrate deposited by chromate conversion technique

XRD analysis of corrosion products

According to XRD results, the formation process of corrosion products may be described as follows, the existence of NaCl accelerates the corrosion as illustrated in figures 13 (a-e). In figures (13a, b, and c), XRD spectra for corrosion products for uncoated AZ91C-Mg alloy specimens immersed in 3.5% NaCl only ,3.5% NaCl + Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (0.2N), and 3.5% NaCl + Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (0.1N) respectively; the resulted peaks indicating reaction of substrates with mentioned media and increased corrosion rate. Figures (13d and e) represented XRD spectra for corrosion products for coated AZ91C-Mg alloy specimens immersed in 3.5% NaCl+Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (0.15N), and coated sample in 3.5% NaCl, pH=1, respectively; the resulted peaks indicating reaction coated substrate with mentioned media and formation of protective oxides and hydroxides and therefore decreased corrosion rate.



(a) XRD analysis for uncoated sample in 3.5% NaCl, pH=6

(b) XRD analysis for uncoated sample in 0.2 N Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>(c) XRD analysis for uncoated sample in 3.5% NaCl+0.1 N Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>(d) XRD analysis for coated sample in 3.5% NaCl+0.15 N Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>

(e) XRD analysis for coated sample in 3.5% NaCl, pH=1

Figure 13. XRD analyses of corrosion product

#### IV. CONCLUSION

On the basis of material presented in this paper the following conclusions can be drawn:

1. Weight loss measurements show that the chromate conversion coating layer can improve the corrosion resistance of AZ91C-Mg alloys.
2. Corrosion resistance of AZ91C using this technique has been enhanced in terms of improved efficiencies ( $\zeta$ ) by different percent as following: 19.6% in 3.5% NaCl at pH=1, 79% at pH= 2, 96% at pH=6, 81% at pH=7 and reaches 84% at pH= 9.
3. Sodium borate (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) was found to be a good corrosion inhibitor, as efficiency improved to 71% at concentration of 0.05N.

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## BIOGRAPHIES

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