

Film Stability on Zn-Al-Cu Alloy in Universal Buffer

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Abstract

The effect of some anions and pH of solution on the corrosion of Zn-Al-Cu alloy were tested by impedance, cyclic voltammetry and scanning electron micrographs in the universal buffer. The tested anions included Cl^- , SO_4^{2-} , IO_3^- , MoO_4^{2-} , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ and CH_3COO^- . In acidic medium (pH 2) $\text{Cr}_2\text{O}_7^{2-}$ produces the highest passivation of the alloy surface, whereas in alkaline medium (pH 12) CrO_4^{2-} is the best passivator. The presence of $\text{Cr}_2\text{O}_7^{2-}$ in the solution produced a smooth surface on the alloy and minimized the number of pits formed in the universal buffer. The most protective film was formed in solutions of pH 9.7. The order of film stability is at pH $9.7 > 7.7 > 12 > 2$.

Introduction

The formation, composition and properties of anodic passive layers on zinc in aqueous media have been the matter of many publications in the last decades, particularly due to the fact that zinc is one of the most important and widely used metallic coatings for corrosion protection of iron or steel under atmospheric outdoor and indoor exposition. Since some components of engines are made with Zn or Zn alloys, corrosion problems are possible. Despite its fairly negative standard electrode potential value, zinc exhibits quite good corrosion resistance in near neutral aqueous solutions or under ordinary atmospheric conditions, because of the formation of stable protective films on the metal surface. Degradation of the protective film in more aggressive conditions can, however, lead to damage. Vernon [1] claimed that the formation of the protective layer on zinc is governed largely by the pH of the environment. Zinc corrodes over a wide range of pH, since it forms cations up to pH 9 and oxyanions under more alkaline conditions [1]. The corrosion of zinc in aqueous environments is inhibited by the presence of chromate ions [2]. Thus galvanized products are frequently treated with formulations based on chromate or dichromate ions to prevent "white rusting" (corrosion product of zinc)

during storage in damp conditions [3]. The anodic behaviour of Zn in borate solutions in absence and presence of Cl^- ions has been investigated by galvanostatic polarization technique [4].

Experimental Details

The Zn alloy was composed of 96.34% Zn, 2.8% Al, 0.86% Cu. The universal buffer had a constant ionic strength (100 ml of mixed acids: 0.04 M phosphoric acid, 0.04 M acetic acid, 0.04 M boric acid adjusted to the required pH by 0.2 M NaOH). Double distilled water was used for the preparation and dilution of all the solutions. Measurements were conducted in unstirred solutions and at constant temperature ($25 \pm 1^\circ\text{C}$). To achieve high reproducibility, the electrode was pretreated always using the same procedure. Before each experiment, the electrode surface was mechanically polished with successive grades of emery papers up to 1200 grit, then washed with acetone, double distilled water and finally with fine tissue paper so that the surface appeared mirror bright.

The electrochemical measurements were all carried using IM6 Zahner electric, Medtechink, Germany. The system is suitable for carrying out the different electrochemical measurements such as: impedance measurements and cyclic voltammetry. Impedance measurements were conducted with excitation amplitude of 10 mV peak to peak. The working frequency range was 0.1 Hz to 100 kHz. The data was fitted to suggest equivalent circuit models and appropriate plot

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formats can be obtained. All the CV experiments were carried out in solutions 5 min after the alloy immersion. The anodic sweep was initiated at -1.4 V, a potential slightly more negative than the open-circuit potential. The cyclic voltammetric measurements were carried out using a scan rate $1 \text{ m}\cdot\text{V}\cdot\text{s}^{-1}$.

SEM studies were carried by JEOL/SM T20 (Japan) scanning electron microscope.

Results and Discussion

Acidic Medium

The effect of $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} , MoO_4^{2-} , IO_3^- , SO_4^{2-} and Cl^- ions on the corrosion processes occurring at the electrode/electrolyte interface was investigated in universal buffer. The impedance behaviour of Zn-Al-Cu alloy after 60 min of electrode immersion in solutions of pH 2 containing 0.01 M additives is presented as impedance plots in Fig. 1a. In all cases, the surface film formed does not possess capacitive behaviour, as indicated by the departure of $\delta\log Z/\delta\log f$ from the theoretical value of -1, which is expected in case of pure capacitive behaviour. However, in case of presence of $\text{Cr}_2\text{O}_7^{2-}$ the slope tends towards the value of -1.

The impedance data of the alloy in the above solutions were analyzed using the equivalent circuit depicted in Fig. 1b. The equivalent circuit consists of R_s , which represents the solution resistance R_p , the polarization resistance and CPE, the constant phase element.

The values obtained for the circuit elements after fitting using the device software are listed in Table 1. As can be observed from these data, Cl^- and SO_4^{2-} did not improve the corrosion behaviour of the alloy; the corrosion resistance for SO_4^{2-} containing solutions remains more or less the same as that measured in the blank solution.

The addition of IO_3^- , MoO_4^{2-} , CrO_4^{2-} , on the other hand, increased the corrosion resistance from 131.3 Ω to 210 Ω , 300 Ω and 1.824 k Ω , respectively, which is equivalent to 37.4%, 56.2% and 92.8% inhibition. The presence of $\text{Cr}_2\text{O}_7^{2-}$ has increased the corrosion resistance to 6.88 k Ω which is equivalent to 98.1% inhibition. It is also noticed from Table 1 that the capacitance of the electrode film has a high value in the solution containing Cl^- ions (215.6 μF) compared to the blank buffer (68.43 μF). Then a gradual decrease in the capacitance is observed reaching the lowest value in the solution containing $\text{Cr}_2\text{O}_7^{2-}$ (1.36 μF).

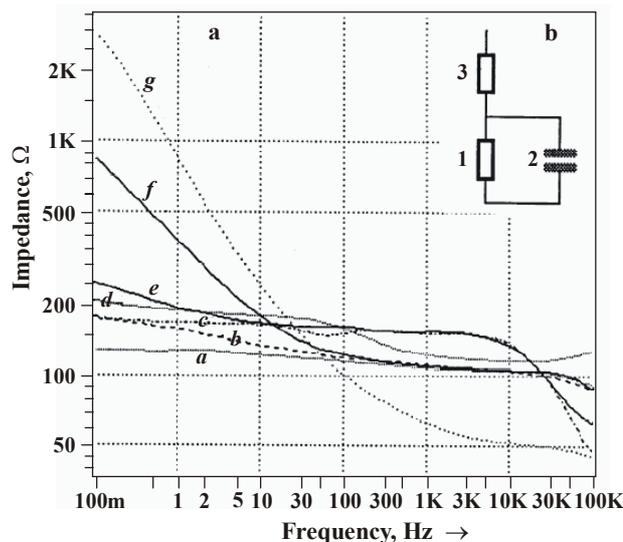


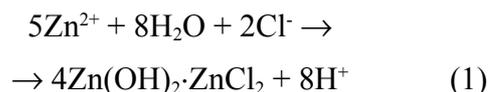
Fig. 1. a – Impedance plots of Zn-Al-Cu alloy in solution pH 2 containing different anions (10^{-2} M), 60 min immersion: (a) Cl^- ; (b) nil; (c) SO_4^{2-} ; (d) IO_3^- ; (e) MoO_4^{2-} ; (f) CrO_4^{2-} and (g) $\text{Cr}_2\text{O}_7^{2-}$. b – Fitted equivalent circuit model: (1) R_p (polarization resistance); (2) CPE (constant phase element); (3) R_s (solution resistance).

Table 1

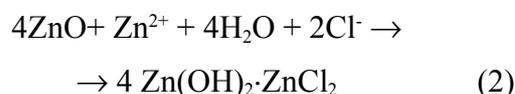
Electrochemical impedance parameters for Zn-Al-Cu alloy in universal buffer of pH 2 containing different additives

	Cl^-	Blank	SO_4^{2-}	IO_3^-	MoO_4^{2-}	CrO_4^{2-}	$\text{Cr}_2\text{O}_7^{2-}$
R_p , Ω	68.88	131.3	133	210	300	1824	6880
CPE, μF	215.6	68.43	26.84	10.35	9.39	2.46	1.36
n	0.933	0.876	0.825	0.867	0.853	0.874	0.855
R_s , Ω	47.61	11.43	26.47	116.2	40.95	100.3	49.69

The presence of Cl^- ions enhances the corrosion due to its aggressive nature. At this pH value and in presence of 0.01 M Cl^- ions, the prevailing zinc species is Zn^{2+} [5]. In presence of Cl^- ions and when the pores are large, Cl^- ions react directly with the cations, thus:



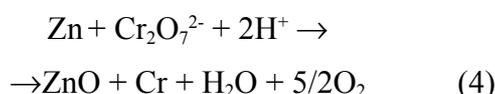
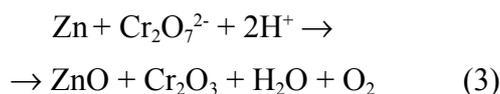
The pH gets lower in the anodic areas, and corrosion can extent toward the zones initially protected by zinc oxide.



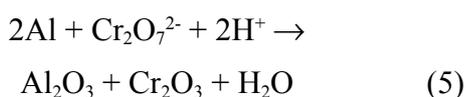
Therefore, the increase in corrosion rate with the addition of Cl⁻ ions is due to the participation of these ions in the metal dissolution reaction. This kind of mechanism has been predicted [6] in the case of Cd and Hg.

The presence of SO₄²⁻ does not change the corrosion resistance; it remains nearly equal to that measured in the blank buffer, *i.e.* 131.3 Ω in blank buffer and 133 Ω in SO₄²⁻ solution. This can be explained on the basis that SO₄²⁻ ions are very similar to the blank buffer as passivators and hence no pronounced inhibition effect of SO₄²⁻ can be measured in the blank buffer solution. The iodate ion does not cause a considerable increase in *R_p*, and therefore is not effective in inhibiting the corrosion of the alloy.

The high *R_p* value in the solution containing the dichromate solution can be attributed to the fact that the dichromate anion acts as a powerful oxidizing agent and is capable of oxidizing the corrosion products to give a stable passive film of Zn, Al and Cu oxides which cover most of the electrode surface according to:



The presence of Al and Cu metals in addition to Zn can form oxide films of Al₂O₃ and Cu₂O, for example, the oxide formed with Al metal is formed according to:

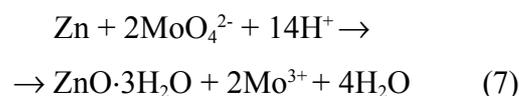
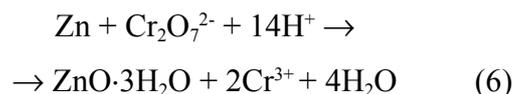


The passive film formed in the dichromate containing solutions was found to incorporate Cr mainly as Cr₂O₃ in the outer layer and metallic chromium in the inner part of the film [7] which increases the corrosion resistance of the alloy surface.

The lower corrosion resistance of the investigated materials in the molybdate and chromate solutions can be attributed to the lower oxidation power of molybdate and chromate compared to that of the dichromate. For example, molybdate cannot oxidize the corrosion sites occurring at the electrode surface as dichromate, and hence a lower percentage inhibition is recorded in the solution containing molybdate.

The passivation action of these anions (Cr₂O₇²⁻, CrO₄²⁻ and MoO₄²⁻) may be better explained by the

involvement of these anions in redox reactions at the electrode surface which leads to the formation of a stable oxide film that increases the corrosion resistance of the alloy. The oxidation-reduction reaction is always preceded by an adsorption step. In this step the passivators adsorb on the material surface especially at the flawed areas of the hydrated oxide covered surface [8]. The powerful oxidizing nature of Cr₂O₇²⁻ and the oxidizing nature of MoO₄²⁻ enhance redox reactions of the type:



The reduction of Cr(VI) to Cr(III) and Cr(0) (*cf.* equations 3, 4 and 6) accounts for the formation of Cr₂O₃ and Cr in the barrier film [9]. These materials are incorporated in the passive film over its whole thickness and cause an increase in the corrosion resistance. Therefore, it must be stated that the inhibition action of Cr₂O₇²⁻, CrO₄²⁻ or MoO₄²⁻ in solutions of pH 2 is based on the incorporation of Cr or Mo in the whole passive film matrix. Chromates are powerful in covering the whole alloy surface by a stable passive film that consists of Zn, Al and Cu oxides. Although molybdate leads also to the passivation of the surface, its inhibition efficiency cannot be compared to that of Cr₂O₇²⁻ since the polymeric nature and partial oxidizing of MoO₄²⁻ cannot fulfill the requirements for the formation of a stable passive film from flawed regions.

According to Pourbaix, molybdate ions in acidic media (1.5 < pH < 4.5) exist in the structure Mo₆O₂₁⁶⁻ or Mo₇O₂₈⁶⁻ [10]. These large polymeric molybdate species are not suitable for accommodation at flawed regions, as does metallic Cr or Cr₂O₃, when chromates or dichromate are used as passivating agents. Thus, formation of Na₃(AlMo₆O₂₆) or Na₆(Mo₇O₂₈) reduces the passivating power of molybdate ions, as compared to either CrO₄²⁻ or Cr₂O₇²⁻.

In highly acidic solutions the chromate ion will be converted to dichromate according to the equation:



which will shift in favor of Cr₂O₇²⁻ at higher acid concentrations. Therefore CrO₄²⁻ (or Cr₂O₇²⁻) are efficient passivating agents. The present results are consistent with this fact.

The values of n recorded in Table 1 are about 0.9, therefore, the CPE is assumed to correspond to capacitive behaviour. The lowest CPE values are recorded in chromate and dichromate solutions, which indicate more protective films. The deviation of n from unity in the present case is related to the inhomogeneous character of the surface [11,12] since n is related to the roughness of the solid surface.

Scanning electron micrographs of Zn-Al-Cu alloy surface after exposure time of 7 days in the blank buffer of pH 2 and in presence of dichromate and chloride ions are shown in Fig. 2(a-d).

When the alloy is immersed in the acidic buffer Fig. 2a and b, it is subjected to both general and pitting corrosion. Deep holes can be easily observed in Fig. 2b, and corrosion products cover the surface.

Visual inspection and optical microscopy showed that the surface of the studied Zn-Al-Cu alloy immersed in the buffer containing dichromate ions was smooth and the pits observed are very minute (Fig. 2c). So dichromate ions prevent the attack of the zinc surface by the corrosive medium (pH 2). This confirms the electrochemical studies which show that

dichromate as a strong oxidizing agent is capable of oxidizing the alloy surface to ZnO, which is responsible for the passive behaviour of the alloy in this acidic medium.

When the chloride ions are added to the acidic buffer, well defined pits are observed (Fig. 2d), whereas no corrosion products are apparent in agreement with the results obtained by impedance studies.

Alkaline medium (pH 12)

The impedance spectra of Zn-Al-Cu alloy in alkaline medium (pH 12) with inorganic additives are presented in Fig. 3 after 60 min of electrode immersion. With the exception of Cl⁻ ions addition of the studied anions caused an increase in the R_p value of the blank buffer. Two peaks in the θ vs. $\log f$ plots indicate that there are two major electrochemical kinetic processes on the electrode surface.

Fitting the data is generated using the equivalent circuit depicted in Fig. 1b. The values obtained for the circuit elements are listed in Table 2.

The impedance spectra recorded for the inorganic anions are characterized by the presence of a low

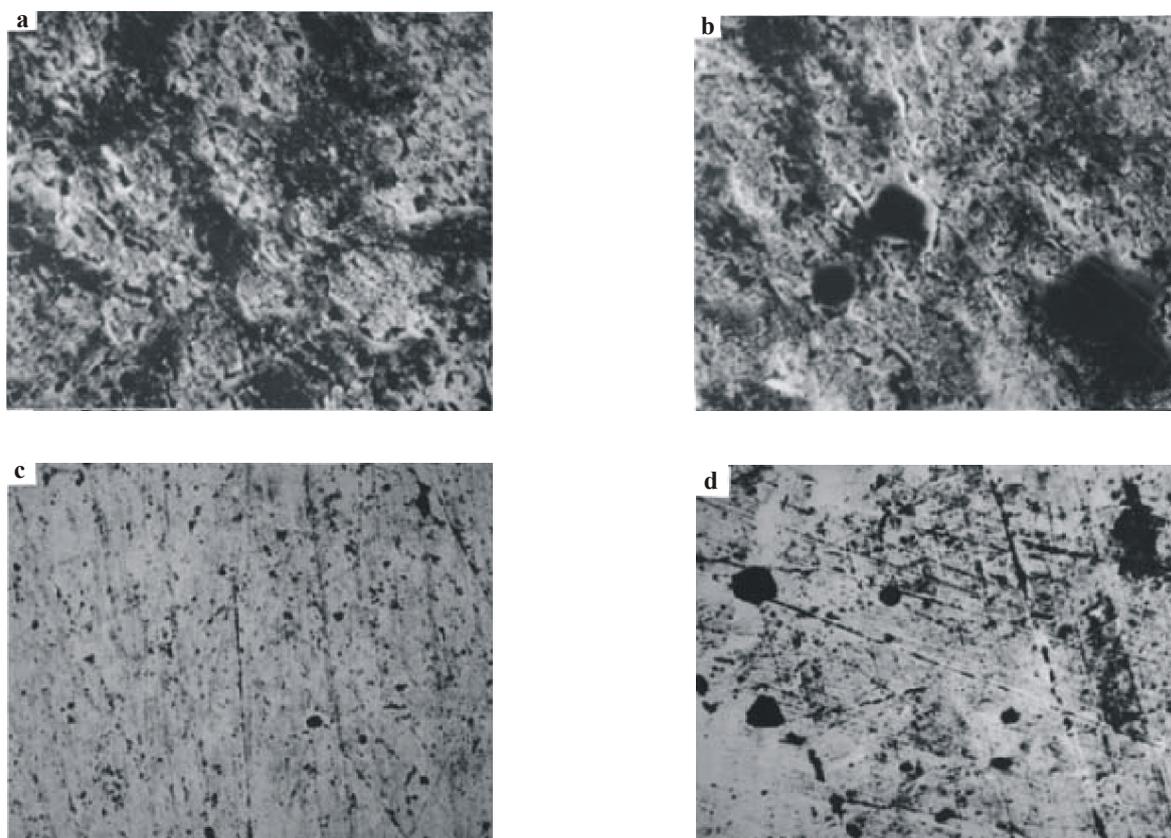


Fig. 2. Scanning electron micrographs of corroded specimens of Zn alloy exposed for 1 week in acidic buffer: (a) blank ($\times 350$); (b) blank ($\times 500$); (c) dichromate ($\times 350$) and (d) chloride ($\times 350$).

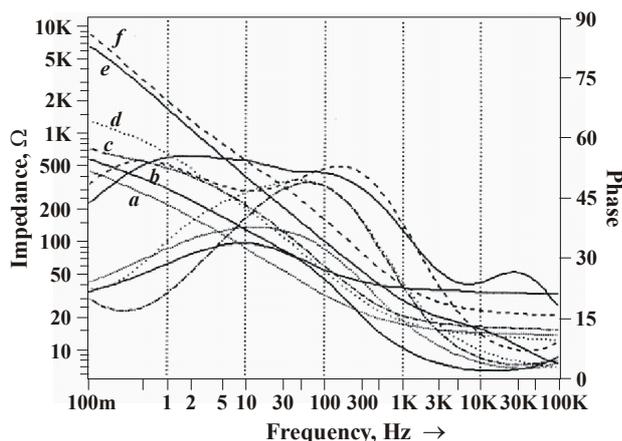


Fig. 3. Bode impedance plots of Zn-Al-Cu alloy in solution pH 12 containing different anions, 60 min immersion: (a) Cl⁻; (b) nil; (c) MoO₄²⁻; (d) SO₄²⁻; (e) Cr₂O₇²⁻ and (f) CrO₄²⁻.

Table 2

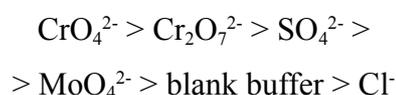
Electrochemical impedance parameters for Zn-Al-Cu alloy in universal buffer of pH 12 containing different additives

	Cl ⁻	Blank	MoO ₄ ²⁻	SO ₄ ²⁻	Cr ₂ O ₇ ²⁻	CrO ₄ ²⁻
R_p , Ω	743.8	832.6	910.1	1582	6450	8410
CPE, μF	23.32	17.48	13.91	10.12	5.784	4.56
n	0.534	0.540	0.659	0.637	0.593	0.64
R_s , Ω	13.39	32.91	15.19	12.57	7.8	10.4

frequency diffusion region, with exponent values close to 0.5, so the processes recorded in the alkaline solution are controlled by diffusion.

Comparison of R_p value in the blank buffer solution or in presence of any of the studied anions with those in solution of pH 2 indicate a major increase in the R_p value. This indicates a higher corrosion resistance of the alloy at pH 12, as compared to pH 2. A protective film, probably consisting of zinc hydroxide [13] is formed.

In presence of Cl⁻ ions the formation of soluble chlorides is the cause in decrease of R_p as compared to the blank solution, thus indicating increased corrosion of the alloy. Sulphate ions, which are not effective inhibitors in acid medium, shows marked inhibition in the alkaline medium. The R_p value on addition of the studied anions is in the sequence:



The presence of CrO₄²⁻ in alkaline solution has a considerable effect on dissolution of the alloy. Chromate is an oxidizing inhibitor and contributes to the formation of a uniform, protective surface oxide film on zinc and its alloys. Chromate has a particular affinity for film formation on the intermetallics, which otherwise are difficult to passivate [14].

In basic solutions dichromates are reduced according to:



This explains the reason why chromates are more effective inhibitors than dichromates at pH 12, as the former directly react with the components of the alloy. The produced Cr(OH)₃ and Cr₂O₃ are present in basic solution as either Cr(OH)₆³⁻ or [Cr(OH)₆H₂O]²⁻ [15].

The low inhibiting power of molybdate at pH 12 is related to formation of the porous Mo(OH)₃, which does not contribute effectively to the surface protection of the alloy.

pH 9.7

The impedance data recorded in the pH 9.7 solution is presented in Fig. 4 after 60 min immersion. The circuit used in the fitting of these data is the same as in Fig. 1b. Table 3 shows the electrochemical impedance parameters for the added anions at pH 9.7.

The exponent of the constant phase element, n , varies between 0.921 and 0.721 due to the inhomogeneous character of the surface [11,12]. This value is an indication that the process is under diffusion control. The higher value of n (0.921) in the blank buffer solution indicates better capacitive properties at pH 9.7, than solutions containing the studied an-

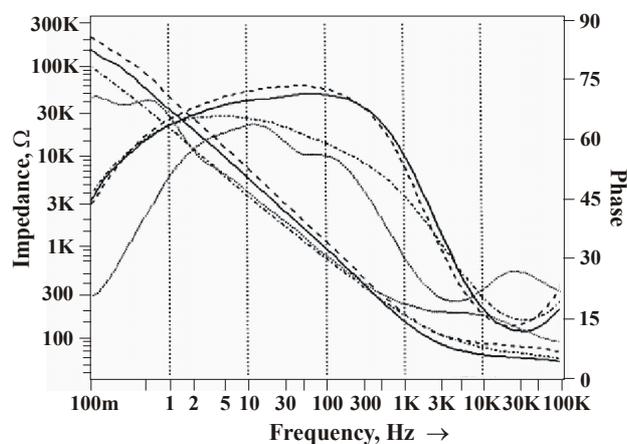


Fig. 4. Impedance plots of Zn-Al-Cu alloy in solution pH 9.7 containing different anions (10⁻² M), 60 min: (···) CH₃COO⁻; (----) Cr₂O₇²⁻; (—) CrO₄²⁻ and (- - -) nil.

Table 3

Electrochemical impedance parameters for Zn-Al-Cu alloy recorded after 60 min in pH 9.7 c containing 0.01 M anions

	Blank	CrO ₄ ²⁻	Cr ₂ O ₇ ²⁻	CH ₃ COO ⁻	SO ₄ ²⁻	Cl ⁻
R_p , Ω	391.8	309.4	292.8	67.44	142.6	27.58
CPE, μF	0.960	1.113	1.28	1.34	1.125	1.007
n	0.921	0.801	0.721	0.709	0.801	0.756
R_{ss} , Ω	69.43	50.88	56.44	113	63.95	42.84

ions. Under these conditions the passive layer on the alloy is highly stabilized. At this pH value, competition in the adsorption process by OH⁻ ions with other anions to form a passive film on the alloy is very limited, this leads to the higher R_p value recorded at pH 9.7 as compared to pH 12.

Comparison of R_p values for the blank buffer solution indicates that the highest recorded value was in solutions of pH 9.7. R_p values are in the order: pH 9.7 > pH 12 > pH 2. The same trend is observed in presence of the added anions, with the exception of Cr₂O₇²⁻ where R_p values at pH 2 and pH 12 do not differ significantly.

An important observation concerning the R_p values is that addition of the studied anions to the buffer does not cause an increase in R_p , but rather a decrease which is quite marked in presence of SO₄²⁻, and more so in presence of Cl⁻ ions. It has been recorded that the presence of Cl⁻ ions in solution can accelerate the dissolution process at any pH; even though the nature of the attack may differ. Even when the oxide film is stable (around neutral pH) extensive local attack is caused by aggressive ions such as Cl⁻ [16], by adsorption in the flawed regions and producing soluble complexes. The results indicate that at this pH, SO₄²⁻ ions also compete with the anions of the buffer solution, causing destabilization of the surface film. The same is observed in case of CrO₄²⁻ and Cr₂O₇²⁻, although their effect is not as destructive as Cl⁻ and SO₄²⁻ ions.

To study the effect of Cl⁻ and SO₄²⁻ ion concentrations, Bode diagrams for the alloy at pH 9.7 were recorded. Figure 5 shows the results in presence of Cl⁻ ions. Table 4 shows the electrochemical parameters after fitting the impedance data which obey the circuit in Fig. 1b. The EIS for NaCl solution was quite similar to that of Na₂SO₄ solution. The same behaviour was observed, the addition of either NaCl or

Na₂SO₄ does not increase the corrosion resistance of the alloy, but a decrease in R_p value is observed. At the same concentration of either Cl⁻ or SO₄²⁻ ions, the R_p value is much lower in case of Cl⁻, indicating that competitive adsorption by Cl⁻ ions is more effective than SO₄²⁻ in producing a surface less resistant to corrosion. Activation of the aluminium surface by SO₄²⁻ ions by competitive adsorption was recorded, where SO₄²⁻ concentration was less than 0.2 M [17].

As the concentration of either Cl⁻ or SO₄²⁻ increases, R_p decreases and CPE increases, indicating a thinner and less protective surface film. Figures 6 shows the results of fitting for Zn-Al-Cu alloy in pH 9.7 containing 10⁻³ M NaCl. Good agreement between

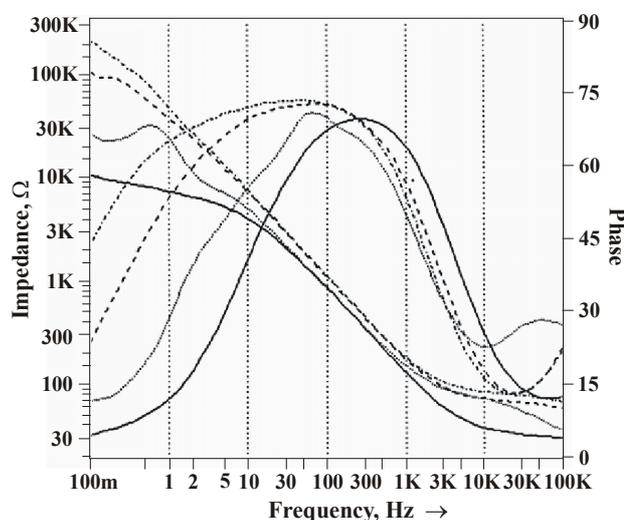


Fig. 5. Bode impedance plots of Zn alloy after 60 min of electrode immersion in solution of pH 9.7 containing different NaCl concentrations (M): (----) nil; (-.-) 10⁻³; (....) 10⁻² and (-) 10⁻¹.

Table 4

Electrochemical impedance parameters for Zn-Al-Cu alloy in universal buffer of pH 9.7 containing chloride and sulphate

	Conc., M	R_p , Ω	CPE, μF	n	R_{ss} , Ω
Blank	0	391.8	0.960	0.921	69.43
Cl ⁻	10 ⁻³	127.5	0.978	0.813	57.82
	10 ⁻²	27.58	1.007	0.756	42.84
	10 ⁻¹	8.223	1.253	0.827	28.99
SO ₄ ²⁻	10 ⁻³	217	0.955	0.815	110.1
	10 ⁻²	142.6	1.125	0.801	63.95
	10 ⁻¹	71.8	1.914	0.795	63.87

the experimental and fitted data was obtained, which supported the validity of the proposed model and the suggested diffusion-controlled process is confirmed as the exponent value is close to 0.7 for both solutions. One can conclude that both SO_4^{2-} and Cl^- anions contribute together in the destruction of the passive film on the Zn-Al-Cu alloy surface at pH 9.7.

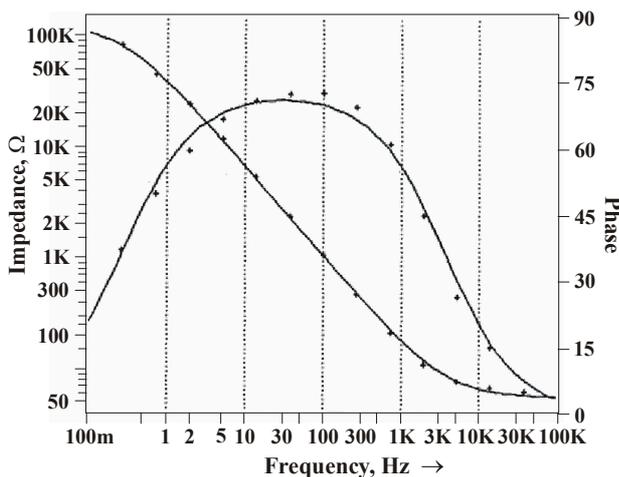
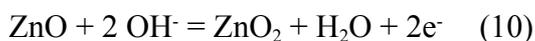


Fig. 6. Bode plot for Zn alloy in buffer (pH 9.7) containing 10^{-3} M NaCl: (x) experimental spectrum and (—) fitted spectrum.

A general survey of the literature indicates that the nature and mechanism of anodic passivation of Zn in alkaline solutions are the subject of debate. It is generally accepted that Zn passivation begins with the precipitation of the zincate ion as $\text{Zn}(\text{OH})_2$ or ZnO [18].

Shams El Din *et al.* [19] and Popova *et al.* [20], observed that ZnO_2 is formed in weak alkaline media only at or very near to oxygen evolution potential according to the reaction:



Near Neutral Medium (pH 7.7)

The electrochemical behaviour of the Zn-Al-Cu alloy was investigated in universal buffer at pH 7.7. Electrode impedance characteristics were found to be affected markedly by the added anions concentrations rather than by electrode immersion time. Typical impedance plots of the alloy after 120 min of electrode immersion in universal buffer solution containing 10^{-2} M concentration of NaCl and Na_2SO_4 were obtained.

At low frequencies, the impedance of blank buffer (pH 7.7) was higher than that of the NaCl solution, and in order, of the Na_2SO_4 solution. This result

clearly expresses the nature of the oxide films formed on the alloy surface. The low impedance of Na_2SO_4 solution therefore is possibly due to the presence of a thin porous oxide film on the alloy surface. The Bode impedance plots showed linear portions at intermediate frequencies. The Nyquist plots of Figure 7 shows depressed semicircles that could be attributed to alloy surface inhomogeneity [21]. The experimental impedance data were fitted to the proposed electronic-circuit model in Fig.1b. The R_p values, estimated from the diameter of the semicircles are in the order: blank buffer > Cl^- containing solution > SO_4^{2-} containing solution.

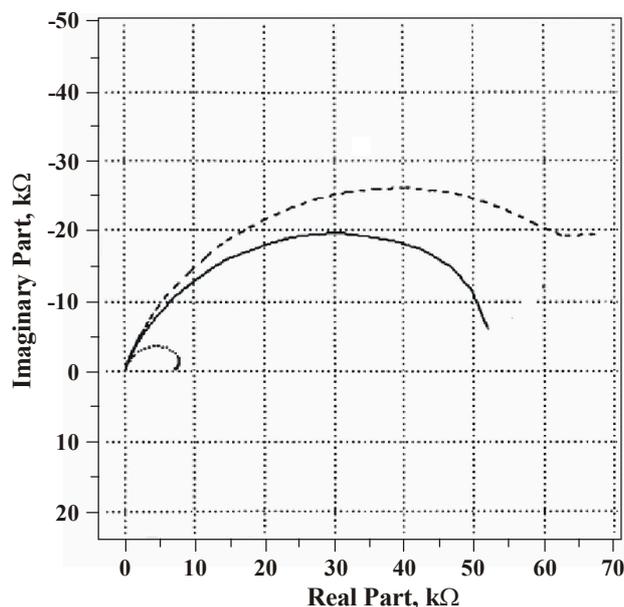


Fig. 7. Nyquist plots of Zn-Al-Cu alloy in solution pH 7.7 containing 0.01 M anions, 120 min: (---) nil; (—) NaCl and (....) Na_2SO_4 .

Table 5 shows the electrochemical parameters for the alloy in 10^{-2} M NaCl and Na_2SO_4 containing solution after 120 min of electrode immersion. It is noticed that the addition of NaCl or Na_2SO_4 increases the corrosion of the alloy compared to the blank solution (pH 7.7). Also, the R_p value is higher in NaCl solution ($R_p = 60.6 \text{ k}\Omega$) compared to Na_2SO_4 solution ($R_p = 9.34 \text{ k}\Omega$). The capacitance values are also in the following order: blank < NaCl containing solution < Na_2SO_4 containing solution, which gives rise to some modification of the passive layer formed in chloride containing solution.

The exponent n shows a value close to 0.7 which is considered to be due to diffusion controlled processes.

Table 5

Electrochemical impedance parameters for Zn-Al-Cu alloy in universal buffer of pH 7.7 containing chloride and sulphate

	Blank	Cl ⁻	SO ₄ ²⁻
R_p, Ω	78.4	60.6	9.34
CPE, μF	681.1	700.5	805.9
n	0.769	0.766	0.724
R_s, Ω	79.88	102.7	50.41

Comparison of the R_p values in the blank buffer at pH 7.7 and 9.7 indicate a lower value in the former case. The formation of a protective layer on zinc is governed largely by the pH of the environment [1]. Zinc corrodes by forming cations up to pH 9 and oxyanions under more alkaline conditions [22]. The present results indicate that the stability of the film formed on the alloy in the blank buffer is in the order of the solution pH value, thus; pH 9.7 > pH 7.7 > pH 12 > pH 2. This indicates that the film is highly unstable at pH 2, due to the abundance of H⁺, as explained previously, while the most protective film is formed at pH 9.7.

The decrease in R_p by addition of Cl⁻ or SO₄²⁻ to the buffer solution at pH 7.7 is due to the incorporation of the anions in the oxide film formed at this pH. Similar results were reported [23] where sulphate ions were found to be incorporated in the oxide film formed on a number of alloys, within the pH range 4 and 9, and out of this range, sulphate ions did not affect the corrosion behaviour of the studied alloys. The contamination of the film by SO₄²⁻ or Cl⁻ ions leads to a relatively higher conductivity of the oxide film, perhaps due to a higher density of film defects. This is the case in the present study, where SO₄²⁻ contamination produces a more defective film than Cl⁻ contamination, at pH 7.7.

Conclusions

Iodate, molybdate, chromate and to a higher degree dichromate ions increase the corrosion resistance of Zn-Al-Cu alloy in universal buffer at both acidic and alkaline pH value, whereas Cl⁻ ion increases the corrosion rate.

In the blank buffer, the stability of the film formed on the alloy is dependent on pH of the solution in the order, pH 9.7 > 7.7 > 12 > 2, *i.e.* the most stable is formed in neutral and weakly alkaline solutions.

Addition of Cl⁻ or SO₄²⁻ decreases the polarization resistance due to anion incorporation.

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