

Full Length Research Paper

ZnO as corrosion inhibitor for dissolution of zinc electrodeposited mild steel in varying HCl concentration

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The corrosion behavior of Zn electrodeposition on mild steel in varying 0.1 to 0.5 M of HCl with and without inhibitor was studied using weight loss measurement and optical microscope. The (OP) results revealed that the corrosion mechanism layers of the zinc plated mild steel without inhibitor has high content corrosivity related to the appearance of cracks due to the dissolution into the acidic medium. However, the zinc electrodeposition with ZnO as an inhibitor in the test medium shows a stable layer formation. The Zn coatings were found to contain an insoluble corrosion products, which act as a corrosion barrier that prevent corrosion from been attacked by the hydrogen presence.

Key words: ZnO, zinc electrodeposition, corrosion, electrochemical, inhibitor.

INTRODUCTION

The use of zinc-plated articles is increasing due to its sacrificial protection of steel from corrosion. This sacrificial protection is due to the fact that the zinc is a less noble metal and cathodically protects the steel even in places where the deposit is damaged. Zinc coatings are obtained either from cyanide, non-cyanide alkaline or acid solutions (Yanjerappa and Thimmappa, 2002). However, zinc is most widely used electrodeposited metal for protecting steel from corrosion. Its corrosion resistance, however, is limited. During the last two decades, efforts to improve the corrosion stability of pure zinc coatings have been directed toward alloying with more noble metal or inducing the environment with inhibitors (Elsherief and Shoebi, 2003).

Since acid solution are widely used in industry, the most important field of application being acid pickling, industrial acid cleaning, acid descaling, oil well oxidizing and manufacturing because of general aggressiveness of acid solutions, the practice and mechanics of inhibitors were engaged to reduce the corrosion attack on metallic materials. Inhibitors are generally used for this purpose to

control the metal dissolution. Most of the well-known inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms. It has been observed that the most of the organic inhibitors act by adsorption on the metal surface (Abd El-Rehim et al., 1999; Abdallah et al., 2008). However, the adsorption mechanism of corrosion inhibitor depends mainly on physio-chemical properties of the molecules such as functional group, character of donating electron and molecular structure (Fayomi et al., 2011). Thus, the aim of this study is to investigate the corrosion behavior of Zinc electrodeposited on mild steel under feasibility immersion into varying percentage of HCl in the presence of Zinc oxide as an inhibitor to mitigate the occurrences of corrosion product in an acidic environment and to improve the corrosion mechanism of the Zinc layer.

MATERIALS AND METHODS

The water used in the preparation of the electrodeposition and corrosion testing solution were purified by a Milli-Q system and analytical grade chemical were used. The steel samples used are of 2.80 x 14. 50 x 20 mm. The test specimen were discaled using wire brush; grind with silica carbide abrasive paper of different grade 120, 240, 320,400 and 1000 grits; well polished to 1 micron,

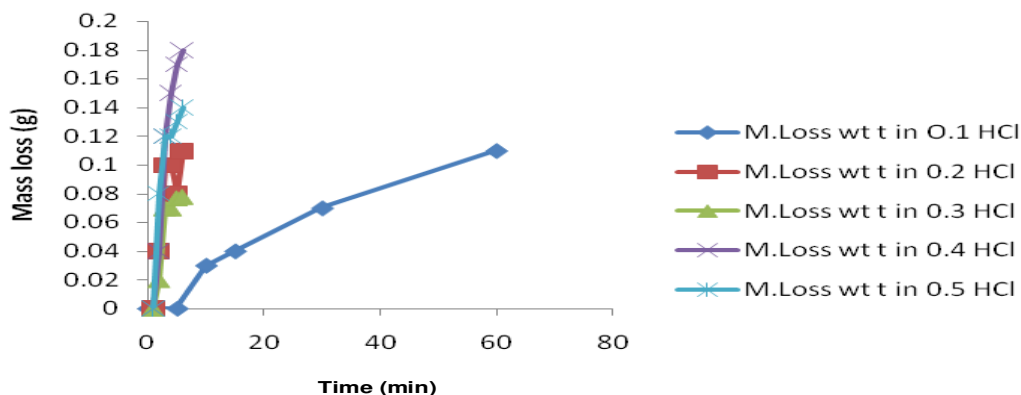
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Table 1. Chemical composition of mild steel before electroplating by optical spectrometer.

C	0.130	Cu	0.036	Sn	< 0.0010	Ni	0.025	Pb	< 0.0030
Si	0.029	Co	0.0057	Zn	0.0230	Mo	< 0.0020	Mg	0.0020
Mn	0.397	Ti	<0.0010	As	0.0059	Al	0.126	B	0.0009
P	0.0067	Nb	0.0046	Bi	0.0025	Zr	<0.0015	La	0.0019
S	0.018	V	<0.0010	Ca	>0.016	Fe	99.2		
Cr	0.0076	W	< 0.010	Ce	< 0.0030				

Table 2. Mass of ZnO required in dissolving each HCl concentration by stoichiometry principle.

S/no	Mole of acid (mole)	Mass of ZnO dissolution (g)
1	0.1	4.0696
2	0.2	8.2390
3	0.3	12.2100
4	0.4	16.2782
5	0.5	20.3410

**Figure 1.** Weight loss-time curves for the corrosion of z- electrodeposited mild steel in varying acid concentration in the presence of inhibitor.

re-cleaned and rinsed in ultrasonic cleaner and the mild still was electrodeposited with Zinc. The Zinc electrodeposited mild steel was employed for the determination of corrosion inhibitor in varying 0.1 to 0.5 molar hydrochloric acid concentration with or without the presence of ZnO. The composition of the base metal sample was analyzed using optical spectrometer (OS) and the results obtained are presented in Table 1 (Popoola and Fayomi, 2011). The concentration of hydrochloric acid in varying 0.1 to 0.5 M for the two separate test medium was set up in 250 ml beaker each for "those with inhibitor and the other without the presence of inhibitor. The stoichiometry ratio and proportion principle was used to determine the exact inhibitor that will take part and form suitable dissolution with the acid, which will also serve as protective layer against corrosion attack. The chemical reactivity ratio was derived from the below relationship.



Hence, one mole of zinc oxide will accurately dissolve in the two

mole of hydrochloric acid solution in 1:2 formations. However, for 0.1 mole of acid, 0.05 mole of ZnO was required. In other to get the mass of zinc oxide in gram, 0.05 mol/l was multiply with the molar mass of zinc oxide 81.39 g/mole to give each value of zinc oxide needed for complete dissolution as show in Table 2. Each mass of inhibitor to the hydrochloric acid concentration under investigation were prepared into 250 ml beaker and the metal sample was immersed into the test medium, at an interval of 5, 10, 15, 30, and 60 min at 303K for the test medium with and without inhibitor with methanol, air dried, and re-weighed. The corrosion rate value was and calculated using Equation 1.

$$R_{\text{corr}} = \frac{\Delta w}{S \cdot t} \quad (1)$$

Plots of weight loss versus the exposure time are shown in Figure 1 and the calculated corrosion rate with time of exposure is noted in Figure 2.

The percentage inhibitor efficiency was determined with the

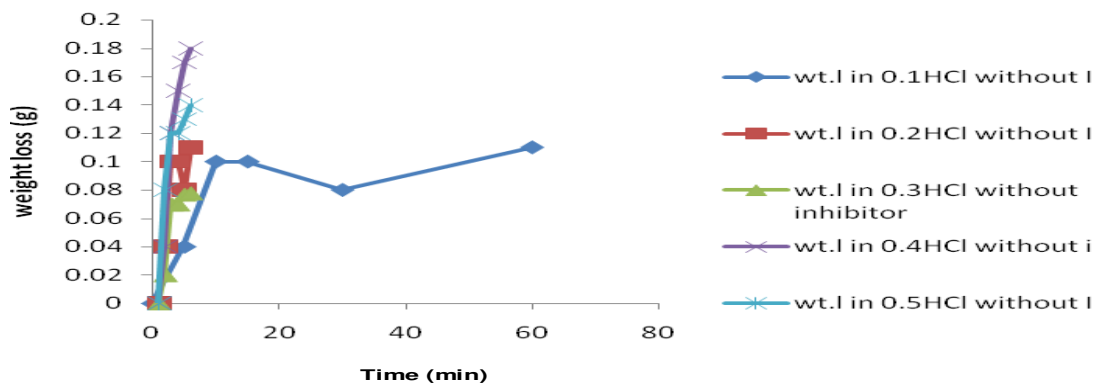


Figure 2. Weight loss of varying concentration of hydrochloric acid in the presence of ZnO proportion.

Table 3a. Weight loss and corrosion rate of zinc electrodeposited mild steel in the presence of inhibitor in acid test medium.

Time (min)	HCl concentration (M)									
	0.1		0.2		0.3		0.4		0.5	
	Mass loss in HCl	Rcorr	Mass loss in HCl	Rcorr	Mass loss in HCl	Rcorr	Mass loss in HCl	Rcorr	Mass loss in HCl	Rcorr
0	0	0	0	0	0	0	0	0	0	0
5	0	0	0.0002	0.0318	0.002	0.3182	0.001	0.1591	0	0
10	0.0011	0.35	0.0005	0.1591	0.002	0.0795	0.0035	1.1139	0	0
15	0.0014	0.6683	0.0005	0.2387	0.002	0.9548	0.0063	3.0076	0	0
30	0.0014	1.3362	0.0007	0.6683	0.003	2.8644	0.0083	7.9248	0.002	1.9096
60	0.0015	2.8644	0.0012	2.2915	0.003	5.7288	0.017	32.4633	0.003	5.7288

Table 3b. Weight loss and corrosion rate of zinc electrodeposited mild steel in the absence of inhibitor in acid test medium.

Time (min)	HCl concentration (M)									
	0.1		0.2		0.3		0.4		0.5	
	Mass loss (g)	Rcorr	Mass loss (g)	Rcorr	Mass loss (g)	Rcorr	Mass loss (g)	Rcorr	Mass loss (g)	Rcorr
0	0	0	0	0	0	0	0	0	0	0
5	0	0	0.04	6.3653	0.02	3.1826	0.04	6.36533	0.08	12.7307
10	0.03	9.548	0.1	31.8262	0.07	22.2788	0.12	38.1922	0.12	38.1922
15	0.04	19.096	0.1	47.7402	0.07	33.4182	0.15	71.6104	0.12	57.2883
30	0.07	66.836	0.08	76.3844	0.077	73.5201	0.17	162.3169	0.13	124.1247
60	0.11	210.055	0.11	210.05	0.078	148.9497	0.18	343.7301	0.14	267.3453

surface coverage. However, hydrogen gas was liberated immediately the zinc electrodeposited steel was immersed at the test medium of the non inhibited solution of hydrochloric acid. Hence, it is appropriate to predict the feasible rate of corrosion and hydrogen evolution in the reacting solution regardless of zinc deposition on the initial substrate metal. Thus, the rate of corrosion can be estimated by the rate of hydrogen evolved and consequently to the degree of degradation that occur to the plated surface without the presence of inhibitor. It is clear to say with the presence of Zinc oxide in this investigation, there is no feasible corrosion taken place on the metal plate.

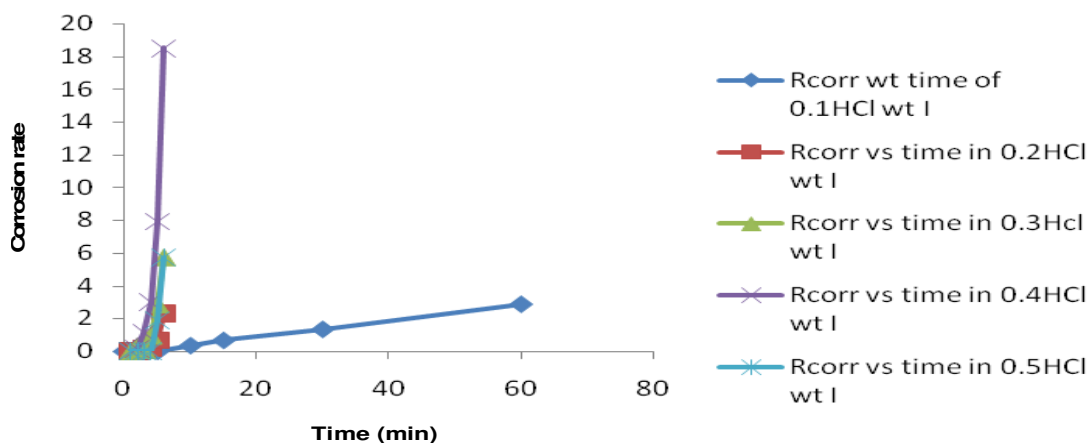
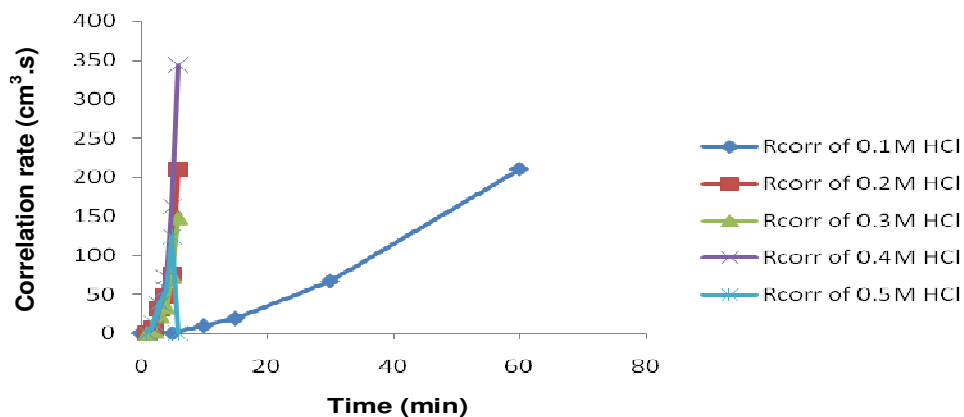
RESULTS AND DISCUSSION

Weight loss measurement

The result examined from the mass loss with time of exposure studies for the zinc plated mild steel specimen immersed in HCl concentration between 0.1 to 0.5 M range set up with and without inhibitor at 303K are presented in Tables 3 and 4. It is noted in Figure 2 that weight loss of Z-D mild steel in the presence of ZnO is

Table 4. Surface coverage and Inhibitor efficiency of zinc electrodeposited mild steel in the presence of inhibitor in acid test medium.

Time (min)	HCl concentration (M)									
	0.1		0.2		0.3		0.4		0.5	
	θ	I.E (%)	θ	I.E (%)	θ	I.E (%)	θ	I.E (%)	θ	I.E (%)
0	0	0	0	0	0	0	0	0	0	0
5	0	0	0.035	3.5	-0.08	-8	0.015	1.5	0.08	8
10	-0.0066	-0.6666	0.095	9.5	0.0414	4.1428	0.093	9.08	0.12	12
15	0.005	0.5	0.095	9.5	0.0414	4.1428	0.108	10.8	0.12	12
30	0.05	5	0.0712	7.125	0.0381	3.8038	0.121	12.1	0.115	11.46
60	0.0963	9.6363	0.099	9.909	0.0395	3.9538	0.085	8.55	0.118	11.87

**Figure 3.** Corrosion rate-time of exposure in varying HCl concentration in the presence of ZnO.**Figure 4.** Corrosion rate- time exposure in varying HCl concentration in the absence of ZnO.

effective as the traces of chemical activity needed to act over the substrate was prevented. Instead, the materials get more surface stability. The amount of hydrogen evolved decrease with the increase in ZnO presence. However, the rate of corrosion is very minimal compare to the test sample without inhibitor as seen in Figure 3. Meanwhile, only specimen with 4.0696 g in 0.1 M acid

strength has unstable surface adhesion and this may be due to the degree of plating on the initial substrate.

In addition, it is vividly observed that the rate of corrosion decreases drastically in the presence of the inhibitor proportion when compare to the control sample as in Figure 4 which contain no inhibitor. The linear illustration indicates the absence of insoluble film that

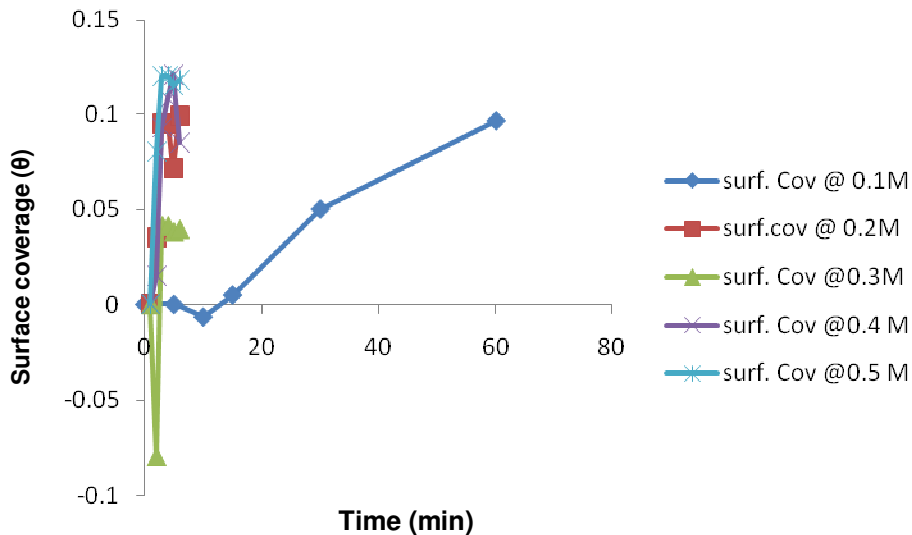


Figure 5. Surface coverage-time curve for the acid concentration in the presence of inhibitor proportion.

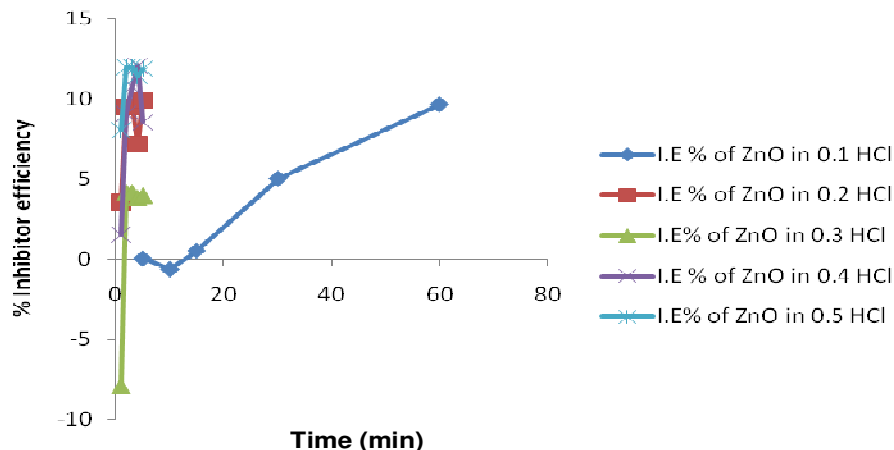


Figure 6. Inhibitor efficiency-time curve for the acid concentration in the presence of inhibitor proportion.

might occur and hence the inhibitors adsorbed onto the surface metal and retard the effective reaction of the corrosion process (Popoola and Fayomi, 2011).

Effect of inhibitor efficiency and the surface coverage

From Figure 5, the presence of zinc oxide in various acid strength concentration varies with time was noted. The film surface coverage was high in all inhibited test medium as layer keep stability and the cohesive bonding of surface film passivation was aligned with substrate except few fume generated between. The degree of surface coverage evaluation was calculated with the

relationship by Ambrish et al. (2010). As shown below.

$$\theta = \frac{w - w_1}{w}$$

Where w1 and w are the weight loss values in presence and absence of inhibitor, respectively. The aligned linearity of the surface coverage ranges from -0.1 to 0.1 signifies the absence of insoluble film during corrosion occurrences, and that the inhibitor adsorbed fusion to the metal surface before impeding the corrosion process. It can also be said from Figure 6, that the weight loss decrease as the concentrations of the inhibitor increased and the surface gain more resistance to corrosion activity

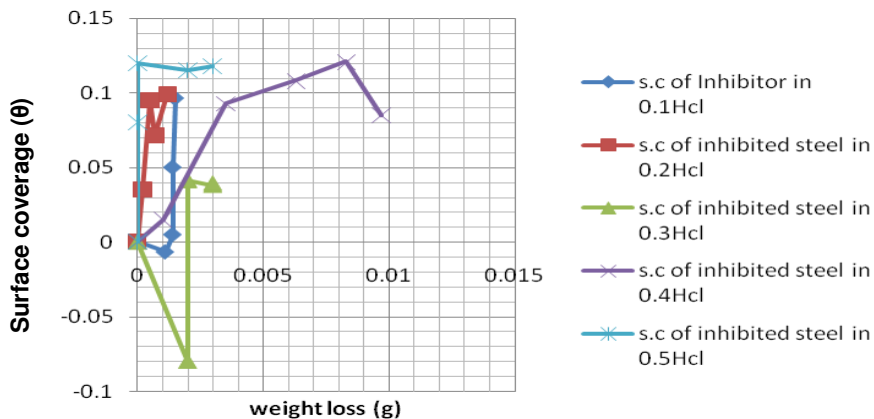


Figure 7. Surface coverage-weight loss plot of inhibited steel in acid medium.

that might speed up corrosion process. In order words, quick surface protection was examined in the acid solution from 0.2 to 0.5 M in the presence of ZnO, than the 0.1 M acid solution which undergoes time trend of about 60 min before full protection. However, zinc oxide is a good inhibitor from this investigation but amongst the concentration of inhibitor used, 25 cm³ showed the lowest effect of reducing the corrosion rate of Z-D mild steel

Effect of varying concentration of inhibitor with time on reaction rate

The studies of relationship between corrosion rate and the volume of hydrogen gas evolved that was deduced by Popoola and Fayomi (2011), implies that as the corrosion inhibitor efficiency increases, the rate of corrosion decrease and the volume of hydrogen gas evolved get lower. With this, corrosion rate is inversely proportional to volume of concentrations induced to the test medium.

$$R \propto \frac{f}{c}$$

$$R = \frac{K}{c}. \text{ Hence } K = RC \quad (1)$$

This means that tripling the inhibitor concentration, reduces the rate of corrosion by one third. In this investigation we consider the effect of concentration on rate of reaction occurring at fixed temperature, so a hypothesis was deduce

$$\text{Rate} = K [C] \quad (2)$$

Thus integrating time of exposure function we sees rate as change in concentration of inhibitor divided by time.

$$\text{Rate} = \frac{\Delta [C]}{\Delta t} \quad (3)$$

An analytical view of Table 3a presented through corrosion rate model above revealed that the concentration of inhibited metal increases with time as the rate of corrosion decreases.

Absorption mechanism

The value of surface coverage θ from the metal-inhibitor interface interaction mechanism for different concentration of the studied inhibitor can be explained by Langmuir adsorption principle and Freundlich isotherm which was best used to determine the θ value for visually all adsorption analysis. The Freundlich expression is given as:

$$\theta = A_c C^{1/f}$$

Where θ = surface coverage
 A = characteristic constant related to the adsorption capacity, C = concentration, f = characteristic constant related to adsorption intensity or degree of favorability of adsorption.

Hence, to determine the $1/f$ slope value, linearity logarithm is used.

$$\log \theta = \log A + \frac{1}{f} \log c$$

The values of surface coverage of the substrate for different concentration of the inhibitor are show in Table 4. However, surface coverage θ was found to increase, with increase in the concentration of the inhibitor. At 300K full absorption influence occurs on the substrate leading to minute loss in weight loss as in Figure 7. Hence, going by Freundlich isotherm principle Figure 5, obey this hypothesis with substrate under 0.1 M HCl with 4.0696 g dissolution.

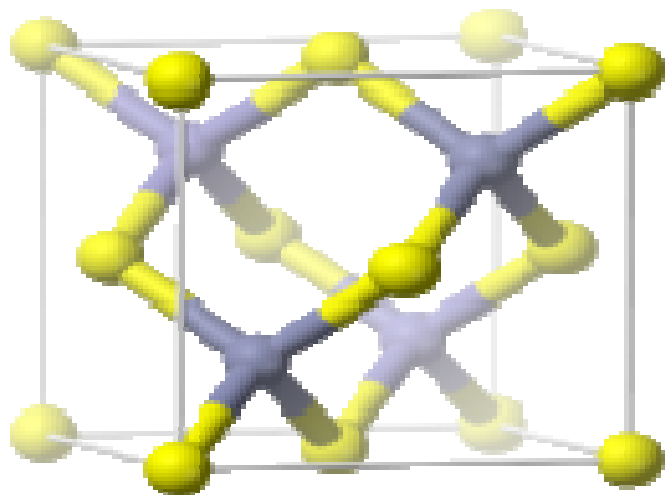


Figure 8. Hexagonal and zinc blende polymorphs.

Mechanism of inhibitor

The reactivity of zinc oxide as an inhibitor on zinc electrodeposited mild steel in varying acid strength composition is a function of several influences such as the crystallization formation, the types of adsorption sites, the metal surface, ability to form complex forms and molecular particles (Fayomi et al., 2011; Abdullahi, 2008).

It is examined that the inhibition mechanism of zinc oxide under studied is feasible due to the insoluble complex formation with ion of mild steel and the zinc oxide. The complex formation is absorbed on the metal surface and hence retarding it from corrosion occurrence. The zincblende form can be stabilized by growing ZnO on substrates with cubic lattice structure. In both cases, the zinc and oxide centers are tetrahedral. The rocksalt (NaCl-type) structure is only observed at relatively high pressures about 10 GPa.

Hexagonal and zinc blende polymorphs have no inversion symmetry (reflection of a crystal relatively any given point does not transform it into itself. This and other lattice symmetry properties result in piezoelectricity of the hexagonal and zincblende ZnO, and in pyroelectricity of hexagonal ZnO (Figure 8) Baruah and Dutta, 2009; Ozgur et al., 2005).

The bonding in ZnO is largely ionic, which explains its strong piezoelectricity. Due to the polar Zn-O bonds, zinc and oxygen planes bear electric charge (positive and negative, respectively). Therefore, to maintain electrical neutrality, those planes reconstruct at atomic level in most relative materials, but not in ZnO - its surfaces are atomically flat, stable and exhibit no reconstruction. This anomaly of ZnO is not fully explained yet.

However, micro structural studies was carried out for z-plated mild steel under optical microscopy (OP) before electrodeposition and after experiment at each stage as illustrated in Figure 9. Basically, three types of phases

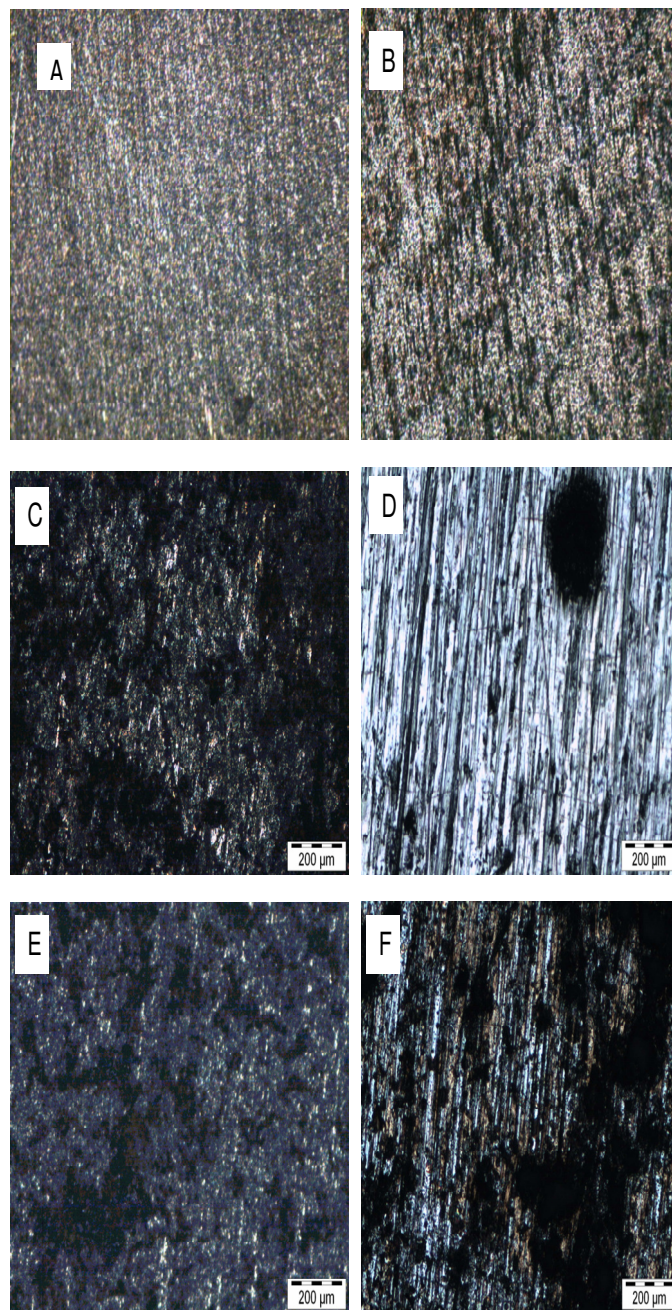


Figure 9. Metallographic micrographs for Z-plated mild steel sample under investigation. (A) micrograph before plating (B) plated sample (C) after immersion into 0.1M of HCl without inhibitor (D) after immersion into HCl with inhibitor (E) after immersion into 0.5 M of HCl without inhibitor (F) after immersion into HCl with inhibitor.

were present. These phases are the α phase which shows as fine dispersed white colour, the second phase with fine dispersed grey colour. It should be noted that these two first phases are the parent phase. The third phase is the inter-metallic phase which shows a coarse black colour and is widely dispersed. Before exposure to the corrosive solution, parallel features on the clean

polished of the substrate surface which are associated with polishing scratches were observed as shown in Figure 9a. Examination of Figure 9b revealed that the metal is protected from corrosion attack. Figures 9c and e, shows corrosion attack (intergranular corrosion) occurs when the specimen is placed in 0.1 and 0.5 M HCl acid without any inhibitor present. (Figure 9d and f respectively) however, corrosion attack is reduced with the Figure 9d show a slight introduction of crack along the alpha –Al phase, Figure 9f show that the alpha phase is present and coarse and no evidence of crack is present. This shows that the inhibitor is effective on the plated sampled mild steel.

Conclusion

Zinc oxide inhibits the plated steel under 0.1 to 0.5 M of hydrochloric variation, thereby allowing the electrodeposited metal under investigation to maintain his protective surface coverage and mitigate the occurrence of corrosion that might occur during chemical reactivity between the metal and the acid. The inhibition efficiency increased as the weight loss reduces with increase in the time of exposure. However, surface coverage stability of this inhibitor is traceable to the adsorption mechanism of insoluble complex on the metal surface.

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