

Effect Of Carbon Doped Aluminium On Corrosion Response Of Galvanised Steel In Seawater

O. I. Sekunowo, G. I. Lawal, S. I. Durowaye, E. C. Igwebuike

Abstract: The uses of galvanised mild steel in many engineering facilities offshore necessitate its protection against all forms of service induced corrosion. This can only be achieved by devising innovative corrosion mitigation measures capable of providing effective and reliable control. Hence, this paper investigates the corrosion propensities of galvanised steel in seawater using specially prepared carbon doped aluminium as sacrificial anode. The 6063 aluminium was doped by adding varied amount of carbon in form of graphite particles to molten aluminium and mechanically stirred vigorously before casting. Then, the commercial galvanised steel and carbon doped aluminium coupons were coupled in a corrosion cell with seawater as the electrolyte. Corrosion simulation lasted seventy days and the data obtained was analysed. Results show that corrosion of the carbon doped aluminium increased with increase in doping of aluminium. The cathodically protected galvanised steel suffered minimal corrosion rate of 4.9×10^{-2} mpy compared with the undoped aluminium anode which exhibited a huge 38.9×10^{-2} mpy corrosion rate. The microstructure before and after corrosion also revealed that surface attack was more pronounced on the carbon doped aluminium relative to the galvanised steel. It thus appears that doping of aluminium with carbon is an effective corrosion mitigation alternative for galvanised steel in seawater.

Index Terms: Carbon Doped Aluminium, Galvanised steel, Corrosion, Microstructure

1. INTRODUCTION

The cost associated with the repair of corrosion damage to mild steel structures is very enormous but the use of adequate corrosion protection systems in harsh environments can drastically reduce the cost. Corrosion is an electrochemical process in which an electric current leaves a structure at the anodic site, passes through an electrolyte and re-enters the structure at the cathodic site [1]. Thus, current flows because of a potential difference between the anode and cathode. The total system made of anode, cathode, electrolyte and metallic connection between anode and cathode is termed a corrosion cell [2, 3]. Corrosion control therefore is a process set up to regulate the rate of corrosion, keeping within acceptable and predictable limits [4]. Hot-dip galvanised mild steel has been found to constitute a cost effective corrosion protection system that can last for several years even in the harshest environments [5].

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For more than 100 years, hot-dip galvanised steel has been utilised extensively to combat corrosion in major industrial environments including petro-chemical, transportation and public utilities. The zinc in the galvanised coating is more corrosion resistant than bare iron and steel because zinc corrodes when exposed to the atmosphere and its corrosion rate is approximately 1/30 of that of steel [6]. Similarly, zinc corrodes at different rates depending on its environment hence; the performance of hot-dip galvanised steel varies from one environment to another. Environments in which galvanised steel is commonly used include indoor and outdoor atmospheres, storage of different chemicals, fresh water, seawater, soils, concrete, and/or in conjunction

with other metals, treated woods, or extreme temperatures [5]. The corrosion protection of seawater equipment and offshore structures can be provided by sacrificial anode or an impressed current cathodic protection system. Although the protection by sacrificial anode is more costly than that by means of an external current source, it is preferred for offshore due to its simplicity, stability and minimal maintenance [7, 8, 9]. Commercial anodes for seawater applications are either aluminium or zinc alloys. Aluminium anode possesses reliable long-term performance, better current and weight characteristics than zinc anode [9]. Thus, aluminium anode can exhibit further improved performance by controlling the alloy composition. Al-Zn-In, Al-Zn-Mg and Al-Zn-Sn alloys are commonly used as sacrificial anodes in marine environments [10, 11]. The performance of aluminium alloys used as sacrificial anodes for cathodic protection in seawater was investigated. The corrosion rate of mild steel in artificial seawater was determined as a function of applied cathodic potential. On the basis of the data obtained, the performance of aluminium anode is strongly influenced by the type and concentration of the alloying elements. Even small amount of In (0.05%) in Al-Zn-In alloy is very beneficial. The effective cathodic protection potential determined for mild steel in artificial seawater was -0.78V [9]. Because hot-dip galvanised steel corrodes at different rate in different environment, the corrosion rate of steel in seawater using carbon doped aluminium as the sacrificial anode is hereby experimentally investigated and presented.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

The major materials employed in this study are commercial samples of 6063 aluminium alloy, mild steel, graphite and seawater. Mild steel samples were machined and cut into (50mm length, Diameter 12mm) and 3mm hole was drilled at the center top for each of the eleven samples. The steel samples were galvanised using the facility at Dorman Long Protection Coating limited, a company in Nigeria. The composition analyses of these materials are presented in Tables 1, 2 and 3.

TABLE 1: Composition analysis of 6063 Aluminium alloy

Element	Al	Fe	Si	Cu	Mn	Zn	Ti	Mg	Sn	Ni
Wt. %	98.683	0.323	0.453	0.002	0.015	0.007	0.011	0.499	0.001	0.006

TABLE 2: Composition analysis of Mild Steel

Element	C	Si	Mn	P	S	Cr	Ni	Zn	Cu	V	Sn	Fe
Wt. %	0.195	0.246	0.458	0.038	0.042	0.005	0.024	0.005	0.014	0.002	0.001	98.452

TABLE 3: Seawater analysis

pH	Temp	Conductivity	Total Dissolved Solids	Salinity	Chloride	Acidity	Iron
8.76	29.3°C	50,600US/cm	36,00mg/L	25,700mg/L	14,238.21mg/L	56mg/L	0.04mg/L

2.2 Carbon doped Aluminium Production

The 6063 Aluminium alloy was melted in a crucible furnace and was properly dislaged while carbon in form of graphite (89.5%C) having 32µm mesh particle size was added before casting in a prepared permanent mould. Prior to casting, the mould was robbed with silica mixed with bentonite before coupling. The same procedure was followed for each of the remaining cast samples. After casting, fettling was carried out to remove flashes and sand particles on the cast. This was followed by sample preparation through cutting into required dimensions (length 50mm, diameter 12mm) while 3mm diameter hole drilled at the center top to ensure firm grip during corrosion simulation.

2.3 Corrosion Simulation Set-up

The initial weights of the test coupons which comprise carbon doped aluminium and galvanised mild steel were taken to the nearest 0.001g on a digital weighing machine (OHAUS Adventurer), degreased and dried in acetone (C₃H₆O). One (1) piece of the control galvanised steel sample was connected with aluminium sample (without carbon) both immersed completely in a plastic container of seawater to simulate the corrosion of the materials within the exposed time frame. There are eleven corriion cell set-up altogether of which one without doping served as the control. The setups were immersed in different plastic containers of seawater and the weight loss of each coupon was determined at intervals of fourteen days for a total of seventy days. After removal, the galvanised steel couponss were held under tap water and the surfaces were scrubbed with a rubber stopper to remove the corrosion products. This was followed by cleaning with acetone to halt the minute electrochemical reactions and to also prevent atmospheric corrosion. Thus, the weight loss within the immersion period was determined as the difference between the initial weight prior to immersion and the final weight after immersion. The corrosion rates were calculated using the relation in equation 1 [12].

$$CPR = \frac{KW}{\rho At} \quad (1)$$

(1) where; CPR = Corrosion Penetration Rate in mils per year (mpy)

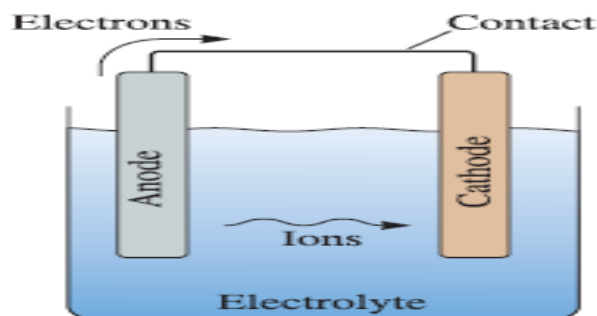
K= constant and its value is 534 for (mil/yr)

W = Weight loss (mg)

ρ = Density of the metal = 7.85 g/cm³ (for mild steel cathode), and 2.7 g/cm³ for carbon doped aluminium anode.

A = Area of the specimen = 2πr(r+h) = 3.33cm² (2)

T = Time of exposure (hrs)

**Fig 1. Corrosion cell setup**

3. RESULTS AND DISCUSSION

3.1 Corrosion rate of Galvanised Steel (Cathode)

The weight-loss and corrosion rates data of the galvanised steel samples are shown in table 4 and illustrated in figures 2 and 3. From figure 2, corrosion rates decrease sharply with increase in exposure time in the entire samples. These are given numerically as 0.973 - 0.389mpy and 0.790 - 0.255mpy for the undoped and doped aluminium anodes respectively while the 1.9 wt. % carbon doped aluminium anode exhibited the least corrosion rate of 0.123 - 0.049mpy within seventy days exposure time. This agrees well with the established characteristics formation of oxide film of aluminium when in contact with seawater [13].

Hence, the oxide film formed by the aluminium was attacked by the carbon which then leaves the system as carbon dioxide thereby aggravating the corrosion of aluminium. The higher the percentage of carbon in the doped aluminium anode, the more aluminium corrodes giving rise to lower degradation rate of the galvanised steel as shown in figure 2. The highest corrosion rate (0.973mpy) was observed in GMS (cathode) connected to undoped aluminium anode apparently due to the absence of doping. Oxide film formed on the aluminium anode inhibits or reduces the rate of supply of electrons to the cathode

thereby encourages the corrosion of the galvanised mild steel samples. Similar influence appears to have been demonstrated by the galvanised mild steel in the formation of zinc oxide film which culminated in corrosion rate reduction. It is observed from figure 3 that the weight-loss increased with the time of exposure. However, GMS_{0%C} exhibited the highest weight loss, 32mg while the lowest weight-loss 4mg, was suffered by GMS_{1.9%C}. The weight-loss behaviour of the galvanised steel coupons was due to the presence of the aggressive chloride ion molecular specie present in the seawater.

TABLE 4: Weight-loss and Corrosion rate (CR) data of Galvanised Mild Steel (GMS) in Seawater

Coupon ID	14th Day		28th day		42th Day		56th Day		70th Day	
	Weight loss (mg)	CR (mpy)	Weight loss (mg)	CR (mpy)	Weight loss (mg)	CR (mpy)	Weight loss (mg)	CR (mpy)	Weight loss (mg)	CR (mpy)
GMS	16.00	0.973	21.00	0.638	26.00	0.527	31.00	0.471	32.00	0.389
GMS0.1	13.00	0.790	15.00	0.456	20.00	0.405	20.00	0.304	21.00	0.255
GMS0.3	12.00	0.730	12.00	0.365	15.00	0.304	17.00	0.258	17.00	0.207
GMS0.5	10.00	0.608	13.00	0.395	14.00	0.284	16.00	0.243	17.00	0.207
GMS0.7	8.00	0.486	9.00	0.274	11.00	0.223	13.00	0.198	14.00	0.170
GMS0.9	7.00	0.426	7.00	0.213	8.00	0.162	9.00	0.137	9.00	0.109
GMS1.1	6.00	0.365	7.00	0.213	7.00	0.142	8.00	0.122	9.00	0.109
GMS1.3	4.00	0.243	5.00	0.152	6.00	0.122	8.00	0.122	8.00	0.097
GMS1.5	4.00	0.243	5.00	0.152	5.00	0.101	7.00	0.106	8.00	0.097
GMS1.7	2.00	0.123	2.00	0.061	4.00	0.081	6.00	0.091	6.00	0.073
GMS1.9	2.00	0.123	2.00	0.061	2.00	0.041	4.00	0.061	4.00	0.049

Note: Coupon identity scheme is given as GMSx where;

GMS-Galvanised Mild Steel and x-wt. %carbon doping in aluminium which ranges from 0-1.

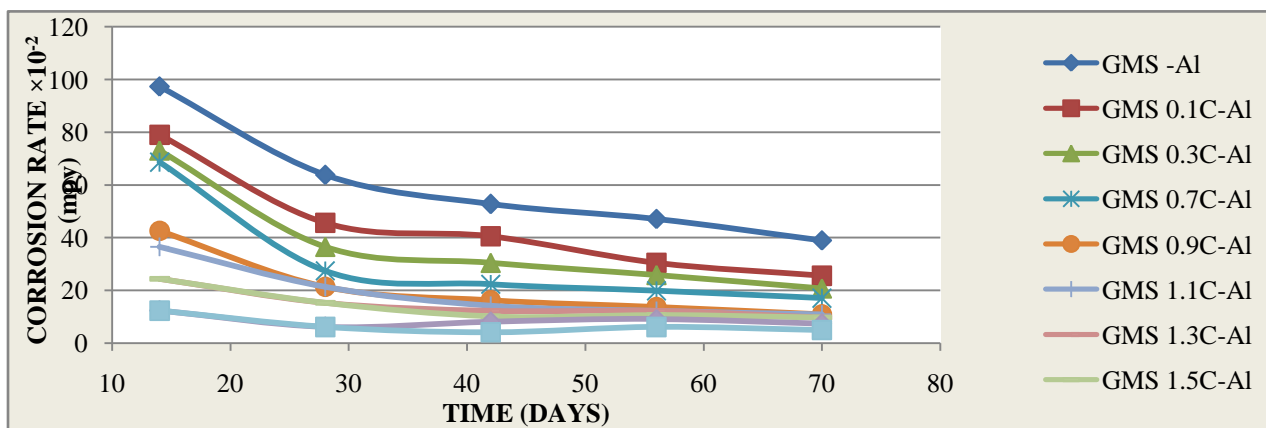


Fig 2. Effect of degree of doping on corrosion rate of Galvanise Steel in Seawater

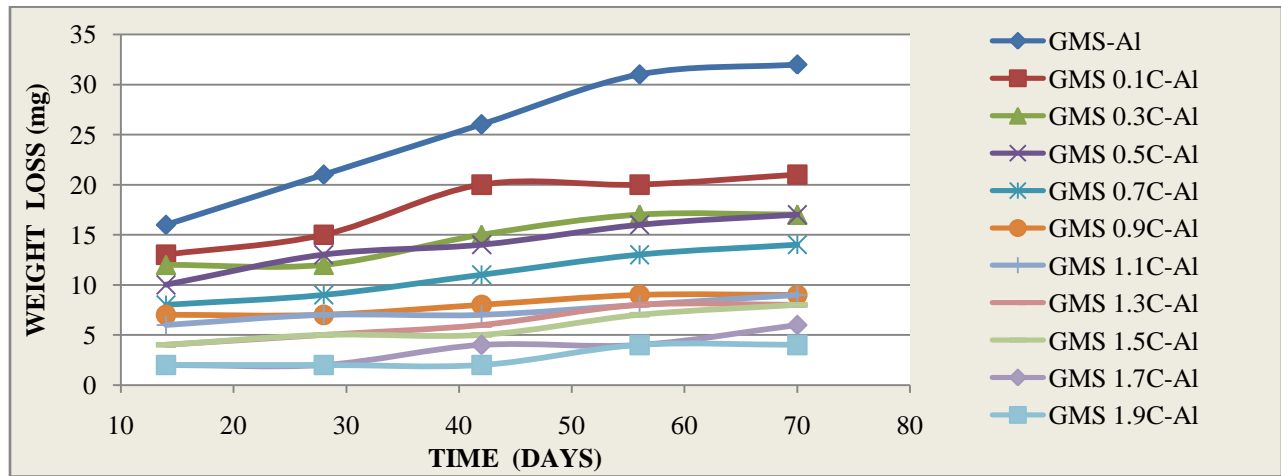


Fig 3. Weight-loss variation of Galvanised Steel within seventy days of exposure

3.2 Corrosion Rate of Carbon Doped Aluminium (Anode)

The weight-loss and corrosion rates data of the carbon doped aluminium anode are presented in table 5 and illustrated in figures 4 and 5 respectively. In comparison with figure 3, the corrosion rate of carbon doped aluminium was by far greater than that of galvanised mild steel. This is due to the reaction of carbon with oxide film on the aluminium surface producing carbon dioxide which attacks the film. The exit of carbon dioxide from the environment

further increases the movement of electrons to the cathode. Hence, the increase in the corrosion rate as the percentage of carbon content increases. This accounts for the reason 1.9% carbon doped aluminium corrodes faster than undoped aluminium. The weight-loss values as plotted on figure 5 corroborate the high propensity of carbon doped aluminium to corrosion given the 38mg weight-loss obtained at 1-9 wt.%C in aluminium. However, the 0% carbon doped aluminium demonstrated the lowest (4mg) weight-loss.

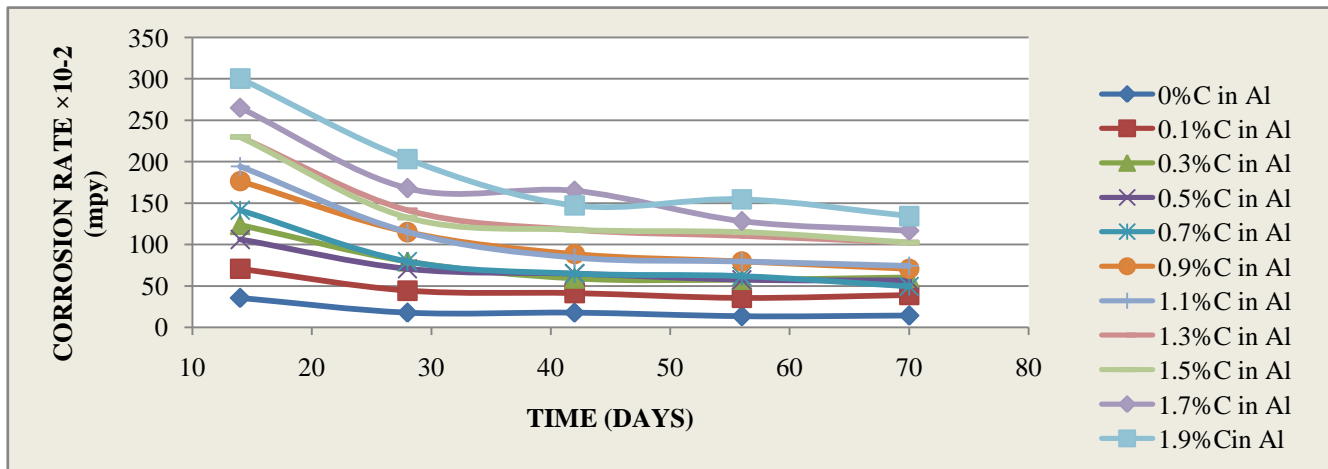


Fig 4. Corrosion rate of carbon doped aluminium in Seawater



Fig 5. Weight-loss variation of carbon doped aluminium in seawater within seventy days of exposure

TABLE 5: Weight-loss and Corrosion Rate (CR) data of Carbon Doped Aluminium in Seawater

Coupon ID	14th Day		28th day		42st Day		56th Day		70th Day	
	Weight loss (mg)	CR (mpy)	Weight loss (mg)	CR (mpy)	Weight loss (mg)	CR (mpy)	Weight loss (mg)	CR (mpy)	Weight loss (mg)	CR (mpy)
Al	2.00	0.354	2.00	0.177	3.00	0.177	3.00	0.133	4.00	0.141
0.1%C in Al	4.00	0.707	5.00	0.442	7.00	0.412	8.00	0.354	11.00	0.389
0.3%C in Al	7.00	1.237	9.00	0.795	10.00	0.589	13.00	0.574	17.00	0.601
0.5%C in Al	6.00	1.061	8.00	0.707	11.00	0.648	13.00	0.574	16.00	0.566
0.7%C in Al	8.00	1.414	9.00	0.795	11.00	0.648	14.00	0.619	14.00	0.495
0.9%C in Al	10.00	1.767	13.00	1.149	15.00	0.884	18.00	0.795	20.00	0.707
1.1%C in Al	11.00	1.944	13.00	1.149	16.00	0.943	18.00	0.795	21.00	0.742
1.3%C in Al	13.00	2.298	16.00	1.414	20.00	1.178	25.00	1.105	29.00	1.025
1.5%C in Al	13.00	2.298	15.00	1.325	20.00	1.178	26.00	1.149	29.00	1.025
1.7%C in Al	15.00	2.651	19.00	1.679	28.00	1.650	29.00	1.282	33.00	1.167
1.9%C in Al	17.00	3.005	23.00	2.033	25.00	1.473	35.00	1.547	38.00	1.343

3.3 Microstructure

Plate 1 shows the micrographs of the as-received 6063 aluminium coupons before and after subjection to corrosion simulation. The microstructure before corrosion (Plate 1a) revealed uniform distribution of coarse Mg_2Si precipitates within the aluminium matrix which depicts the normal wrought aluminium structure. However, after the aluminium has been subjected to corrosion, the microstructure's texture appears to have been significantly eroded (Plate 1b). At the instance of doping with 0.5 wt. % carbon, the Mg_2Si precipitates assumed a rod-like morphology but evenly dispersed within the matrix (Plate 2a). This structure after corrosion suffered texture distortion and erosion of its matrix as shown in Plate 2b. The microstructures of the 1.5

wt. % carbon doped aluminium are presented in Plate 3 (a and b) while Plate 4 (a and b) shows that of 1.9 wt. % carbon doped 6063 aluminium coupons. It is observed that the fractions of Mg_2Si precipitates increase with increase in degree of doping. This may be due to the enhanced coherency provided by carbon for the Mg_2Si precipitates thereby enabling the development of more stable precipitates. However, the coupons in each case show microstructures whose textures have been compromised coupled with severe dissolution of the secondary phase within the matrices. These adverse occurrences affected the materials retrogressively as the degree of doping increases. This is demonstrated by the micrographs in Plate 3b compared with Plate 4b ditto Plate 2b compared with Plate 1b respectively.

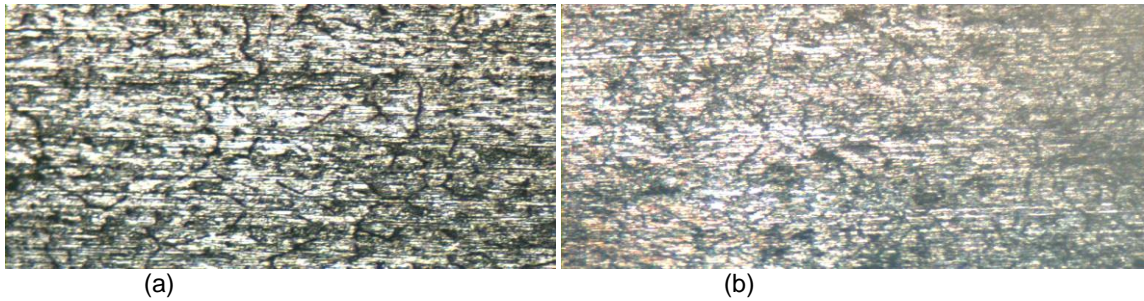


Plate 1: Micrographs of pure 6063 aluminium coupon (a) Before corrosion and (b) After corrosion simulation

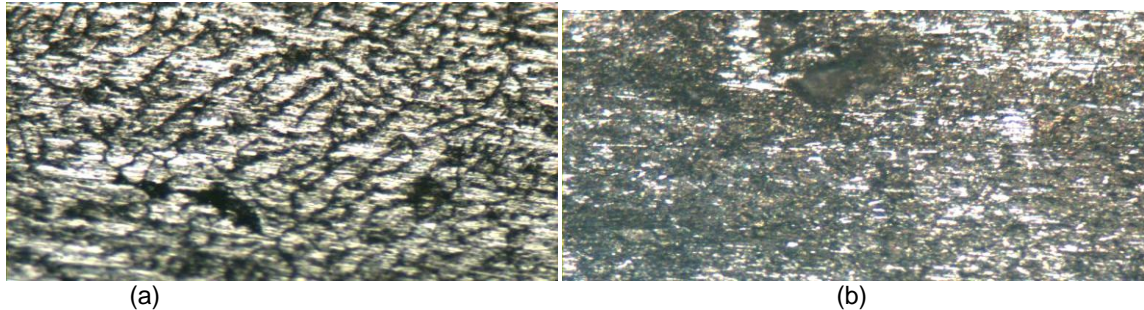


Plate 2: Micrographs of 0.5 wt.%C doping in 6063 aluminium coupon (a) Before corrosion and (b) After corrosion simulation

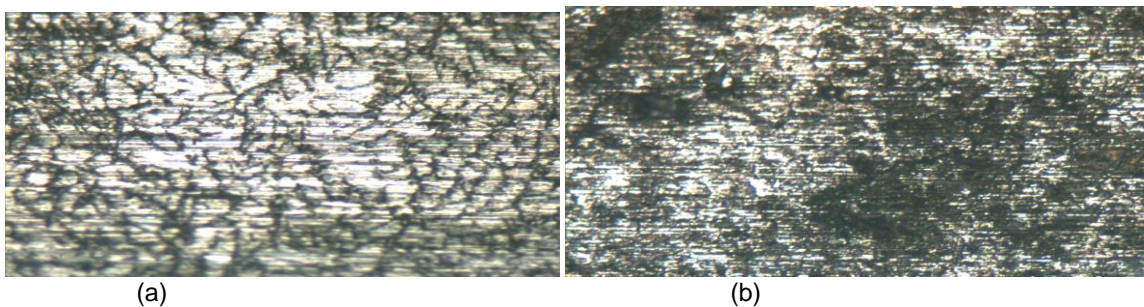


Plate 3: Micrographs of 1.5 wt.%C doping in 6063 aluminium coupon (a) Before corrosion and (b) After corrosion simulation.

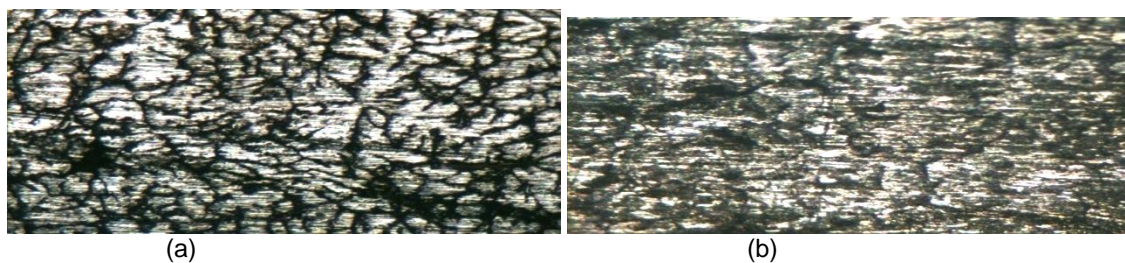


Plate 4: Micrographs of 1.9 wt.%C doping in 6063 aluminium coupon (a) Before corrosion and (b) After corrosion simulation.

4. CONCLUSION

The imperative for an effective corrosion mitigation technique of structures in seawater environment is further established by the results of this study. Corrosion of the carbon doped aluminium in preference to the galvanised mild steel was rather severe which indicates that carbon doped aluminium is a good sacrificial anode for the cathodic protection of galvanised mild steel in seawater. The higher the percentage of carbon in the aluminium anode, the more the corrosion susceptibility of aluminium, giving rise to low corrosion rate of the galvanised steel. Given the microstructural integrity rating of the materials after

corrosion simulation, it is concluded that the effects of corrosion transcend the surface appearance of a material but extend to its internal structures with grave potentials for performance impairment and sudden failure in service.

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