

# Corrosion Characterization of as – Cast Commercial Al – Based Alloy System in Selected Aqueous Media

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## ABSTRACT

*Corrosion characterization of commercial as – cast Al - based alloy has been studied in 0.1M HCl and seawater respectively. The general corrosion trend of passivating metals which aluminium belong to are generally observed but with markedly severity in the acidic environment. This behavior is attributed to the increasing electrical conductivity of the solutions; a consequence of increasing solubility of the media which progressively increased before declining due to the immobility of current carrying ions. The stress – strain test showed that there is a direct relationship between the alloy composition and, the loading force and yielding points. The microstructure analysis carried out via the optical micrographs reveal that the corrosion trend is generally homogeneous with absent of pitting or any form of localized attack in all the samples.*

**Keywords:** Al – based alloy, HCl, Seawater, Corrosion, Passivation, Microstructure.

## INTRODUCTION

As a consequence of the economics of not only production but also of environmental impact and ecological factors [1], excellent strength-to-weight ratio [2], and good electrical and thermal conductivity with high corrosion resistance in pure state and under service conditions [3], it is becoming increasingly important to consider the “cradle – to – grave” life cycle of (light) materials relative to the overall manufacturing process. This utmostly necessitated the recent increase in research of the behaviour of aluminium alloys (and other light metals) subjected to different environments towards the end of the last decade.

The ability of aluminium and its alloys to form barrier oxide micro – film: alumina (Al<sub>2</sub>O<sub>3</sub>) in most environments which has affinity for oxygen, coupled with excellent corrosion resistance has made it one of the primary metals of commerce. Also, in environments harbouring aluminium (and some of its alloys), this film assists in the formation of passive surface layer bonded strongly to its surface which, is stable in aqueous media within pH range of about 4.0 and 8.5, and if abraded, re – forms almost immediately in most environments [4].

There are diverse uses of aluminium and its alloys in the industry and in different environments. Thus, the 0.1M HCl represents the acidic environment while the seawater, which contains the aggressive chloride ion, is of practical importance because, it is present in large amount both in seawater, road salts, and some soils and in lower

concentration in other natural sources where aluminium (and /or its alloys) are frequently used. Thus, the need to understand the corrosion and loading behaviour of Al –based alloys in these environments that are positively acidic and saline respectively.

The microstructure analysis of materials reveal the actual grain boundary distribution of the sample being characterized as the effects of various constraints (here corrosive environment) can easily be seen from the morphology of the optical micrographs. The need for this in material analysis is generally known as it is a vital tool in actual material selection especially for outdoor purposes where stress corrosion cracking and embrittlement are major factors.

In corrosion analysis, failure has been linked to have its origin in the metallurgical history of the material and partly on the media concentration [1]. Hence, in the present study, we will apply both the microstructure analysis and the tensile strength (deformation) test to ascertain how these contribute to the overall observed corrosion trend in the alloy.

Corrosion measurement involves the application of various techniques to determine the corrosiveness of the environment and the rate of metal loss. Corrosion measurement is usually a quantitative method of evaluating the performance and effectiveness of corrosion control and prevention techniques [5]. After evaluation is completed, the result obtained is used to improve and enhance the techniques [6]. The rate of corrosion due to direct attack can usually be estimated from relatively simple laboratory test in which small specimens of the related materials are exposed to a well-simulated actual environment with frequent weight change and dimensional measurements carefully taken. The corrosion penetration rate (CPR) is usually expressed in mm/yr and may be calculated as:

$$C P R = \frac{87.6 \Delta W}{\rho A t} \quad (1)$$

where *CPR* is the rate of corrosion penetration in mm/yr,  $\Delta W$  is the weight loss in milligrams; *A* is the exposed specific area of the specimen in square centimeter,  $\rho$  is the density of the specimen in grams per cubic centimeter and *t* is the exposed time in hours [1,7,8]. The use of this corrosion rate expression in predicting corrosion penetration in actual service is usually successful if the environment has been properly simulated in the laboratory [9] and the corrosion form homogeneous otherwise, it becomes somewhat erratic with local instability [1,2,4].

## EXPERIMENTAL PROCEDURE

**Materials and Method:** The weight loss technique which is a destructive method has been applied in the corrosion characterization of commercial aluminium based alloy systems in 0.1M HCl and Seawater.

The materials used for this work were procured from First Aluminium Plc., Port Harcourt, Rivers State, Nigeria. The digital analytic weighing machine X21-0014 KERN770-15, 15402301 which measures up to 0.00001g was used to weigh the sample before and after immersion to obtain the weight loss.

**Sample and Environment Preparation:** The strips of the materials were cut into coupon sizes of dimension of about  $30\text{mm} \times 10\text{mm} \times 1\text{mm}$  and initial surface area of about  $6.80\text{cm}^2$ . Each sample coupon was pierced with a scribe to provide holes (of negligible dimensions) for the suspension of the strings in the various environments. The surface of each of the coupon specimen was thoroughly polished with emery clothes of 500, 1000, 1200, and 2400m grades as to remove any oxide layers, carbonized layer, and any initial treatment(s) given to the alloy using ASTM standard.

The samples were coded **A** and **B** respectively. The initial weight of each of the sample coupon was carefully measured using a highly sensitive digital analytic chemical weighing machine.

**Simulation of Environment:** The acidic environment (0.1M HCl) for this work was prepared using the normal procedure from pure assay of 36.5% HCl while the seawater environment is a natural source from one of the tributaries of Atlantic Ocean in Port Harcourt, Rivers State, Nigeria.

**Experimentation:** The 24 test coupons were divided into four groups of six in each of the two (2) concentration media. A set of coupon was withdrawn 120 hourly, washed with distilled water, cleaned with acetone and dried in open air. The final weight of each of the test coupon was determined using the digital analytic weighing balance as to enable calculation of the corrosion penetration rate from the weight difference. The tensile strength of the as – cast alloys were carried out at room temperature after the various samples has been treated as outlined above in a screw – driven testing machine at crosshead speed of 0.2mm/min. The chemical composition of the commercial Al – based alloys were subsequently determined.

**Determination of Microstructures:** The corrosion coupons, having been exposed to the respective environments and subsequently re – weighed, were then taken to the Metallographic Laboratory of the Nigerian Metallography Development Council (NMDC), Jos, Plateau State, Nigeria where they were subjected to the normal routine procedure for metallographic analysis for the purpose of producing the microstructures (optical micrographs) for subsequent analysis.

## RESULTS AND DISCUSSION

Table 1 show the chemical composition of the various Al – based alloys being characterized while Tables 2 and 3 shows the corrosion rate data for the various alloys in the environments being studied. Figures 1 – 3 are the graph of the loading force ( $N$ ) against extension ( $mm$ ) for the control samples, samples in seawater and samples in 0.1M HCl in that order. Plates 1 – 14 (with the first two being control) are the micrographs for the various alloys in the environments being studied showing the trend and how the grain boundary of the alloys were affected.

### Corrosion Rate Profile

**Seawater:** From table 2, it can be seen that the usual trend of passivating metals were obeyed with somewhat parabolic trend. There was no system agitation and so the passive film firmly protected the metal surface leading to decreased corrosion rate over the exposure time.

**Acid:** From table 3, it can be observed that all the alloy samples obeyed the usual trends associated with passivating metals. A critical examination of the trends show that the degree of severity was higher in sample **B** than **A**. However, all the samples exhibited CPR values which are within the permissible theoretical values. The setting in of passivation phenomena at about the 600h exposure time may be attributed to the adsorption of  $Cl^-$  on the surface of the alloy due reduction in halide – accelerated dissolution.

### Mechanical Analysis

Figures 1 – 3 show the ultimate strength against the elongation of the alloys at room temperature. It could be seen that the normal stress – strain curves for relatively ductile materials, to which aluminium belongs, were followed by all the samples in each of the media studied though with varying degree of severity.

**Strain Behavior:** A critical look at the curves shows that for the controls (fig. 1), sample **A** fractured at an extension of 3.60mm while sample **B** fracturing at an extension of 2.40mm. In acidic environment (fig. 2), both samples could only extend up to 2.00mm while in the seawater environment (fig. 3), sample **A** extended up to 2.40mm but sample **B** showed somewhat lower value of 2.00mm. These behaviours suggest that there is a direct relationship between corrosion media and strain such that the presence of embrittling species in a corrosion medium reduces the ductility of the material. Also, the higher extensions exhibited by sample **A** as against that of sample **B** supports the claim that impurity atoms diminish the corrosion resistance of aluminium in aqueous media and hence strain resistance. Thus, there is a direct relationship between the alloy composition and its strain behaviour.

**Stress Behavior:** In material characterization, maximum force to failure of samples is a very vital tool to the general adaptation of the material especially in structural application. It can be inferred that the impurity had significant effect on the tensile properties of the alloy. Sample **A** failed at 1395.00N, 1410.00N and 1081.25N for the control, seawater and acid environment respectively. Sample **B** failed at 1275.00N, 1237.50N and 1062.50N in the same order.

In comparative terms, sample **A** appear to be more ductile and relatively easier to be drawn than sample **B**. The important of this is that strain hardening set in and progressively increased as the samples were drawn in the order

**A** and **B**, which may have resulted from the percentage of impurity in the samples. This is reasoned from the point of view that zinc and other impurities settled along the grain boundaries and interfere with dislocation movements thereby causing strain hardening.

### Microstructure Characterization

A cursory look at the photomicrographs (produced at  $\times 125$  magnification) show that the samples in both environments: acidic medium and seawater were significantly affected by corrosion attacks which penetrated into the internal structure of the alloys. The morphologies show attacks that are of the general corrosion type, which was uniformly distributed over the entire surface. There was no noticeable evidence of pitting or localized corrosion attacks. The obvious implication of this observation is that the alloys formed very strong passive films that were chemically stable and widespread over the surface of the samples, hence providing high resistant against penetrations or perforations by corroding species in the media. It can be inferred that as the exposure time increase, the precipitation of the samples also increase. This can be seen from the grain boundary distribution which increased with exposure time.

However, the attacks were most severe in sample **B** than **A** in both environments being characterized. This again supports the fact that impurity atoms diminish the corrosion resistance of aluminium. As would be expected, the samples exposed to the acid medium were more prone to attacks than those in seawater. Generally, theoretical assertions suggest that the presence of halides in seawater normally accelerates pitting corrosion because they have the potentialities of penetrating through the passive film creating perforations in the material. The absence of such perforations or pitting sites in this study suggest that the material formed passive films ( $\alpha$  – alumina) that were resistant to the effects of halides, which are imperative constituent of known seawater.

### CONCLUSION

The corrosion penetration profile of the alloys in all the media were relatively low and found to be within the range of the acceptable CPR values for material application. This is due to the formation of oxide film of alumina ( $\alpha - Al_2O_3$ ) on the interface of the samples and the media due to passivation phenomena.

From the mechanical analysis, the stress – strain relation reveal that the presence of impurity atoms (see table 1) indeed improved the deformation characteristics of aluminium even in harsh corrosion environments especially its ductility. From the photomicrographs, it can be observed that there were no localized or pitting corrosion attacks in

the samples as they generally showed homogeneous corrosion trend. This is evident from the distribution of the

grain boundaries. The chemical compositional analysis of the samples show that the higher the impurity atoms, the higher the corrosion kinetics. This is evidently true from theory that the presence of impurity atoms in pure aluminium though may improve its other technological properties but generally diminishes the corrosion resistance.

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Table 1: Chemical Analysis Data of the Al –Based Alloys

| Sample | Si      | Fe      | Cu      | Mn      | Mg      | Zn      | Ti      | Cr      | Ni      | V       | Pb      | Al      |
|--------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| A      | 0.20726 | 0.48623 | 0.04167 | 0.08050 | 0.01398 | 0.18574 | 0.01568 | 0.00282 | 0.00540 | 0.00493 | 0.02124 | 98.9345 |
| B      | 0.35979 | 0.55400 | 0.09700 | 0.06735 | 0.01819 | 0.29370 | 0.01156 | 0.00367 | 0.00655 | 0.00521 | 0.02649 | 98.5575 |

Table 2: Corrosion rate data for the various Al-based alloys in 0.1M HCl environment

| Time (Hrs)        | Initial Wt. (mg) | Final Wt. (mg) | Wt. Loss (g) | CPR (mm/yr) |
|-------------------|------------------|----------------|--------------|-------------|
| <b>Al-2.5% Zn</b> |                  |                |              |             |
| 120               | 0.3142           | 0.3080         | 0.0062       | 0.2456      |
| 240               | 0.3428           | 0.3312         | 0.0116       | 0.2298      |
| 360               | 0.3252           | 0.3054         | 0.0198       | 0.2614      |
| 480               | 0.3445           | 0.3115         | 0.0330       | 0.3268      |
| 600               | 0.3377           | 0.2804         | 0.0573       | 0.4540      |
| 720               | 0.2971           | 0.2183         | 0.0788       | 0.5203      |
| <b>Al-4.5% Zn</b> |                  |                |              |             |
| 120               | 0.4221           | 0.4149         | 0.0072       | 0.2852      |
| 240               | 0.4003           | 0.3844         | 0.0159       | 0.3149      |
| 360               | 0.3914           | 0.2778         | 0.1136       | 1.5000      |
| 480               | 0.3749           | 0.1987         | 0.1762       | 1.7450      |
| 600               | 0.4131           | 0.2436         | 0.1695       | 1.3429      |
| 720               | 0.3837           | 0.3059         | 0.0778       | 0.5137      |

Table 3: Corrosion rate data for the various Al-based alloys in seawater environment

| Time (Hrs)        | Initial Wt. (mg) | Final Wt. (mg) | Wt. Loss (g) | CPR (mm/yr) |
|-------------------|------------------|----------------|--------------|-------------|
| <b>Al-2.5% Zn</b> |                  |                |              |             |
| 120               | 0.2804           | 0.2790         | 0.0014       | 0.0555      |
| 240               | 0.3450           | 0.3432         | 0.0018       | 0.0357      |
| 360               | 0.3153           | 0.3144         | 0.0009       | 0.0119      |
| 480               | 0.3331           | 0.3323         | 0.0008       | 0.0008      |
| 600               | 0.3138           | 0.3128         | 0.0010       | 0.0008      |
| 720               | 0.3326           | 0.3314         | 0.0012       | 0.0008      |
| <b>Al-4.5% Zn</b> |                  |                |              |             |
| 120               | 0.4228           | 0.4213         | 0.0015       | 0.0594      |
| 240               | 0.4111           | 0.4090         | 0.0021       | 0.0416      |
| 360               | 0.3528           | 0.3511         | 0.0017       | 0.0224      |
| 480               | 0.3641           | 0.3628         | 0.0013       | 0.0129      |
| 600               | 0.3918           | 0.3904         | 0.0014       | 0.0111      |
| 720               | 0.3904           | 0.3890         | 0.0014       | 0.0092      |

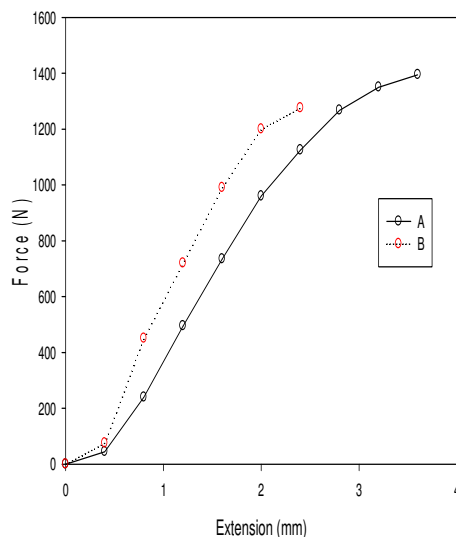
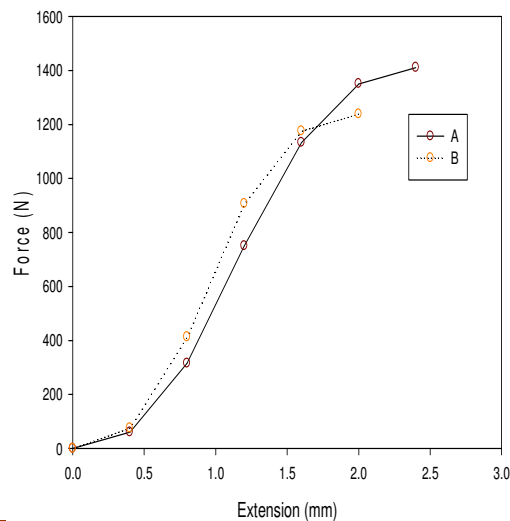


Fig. 1: Force against extension graph for the control samples



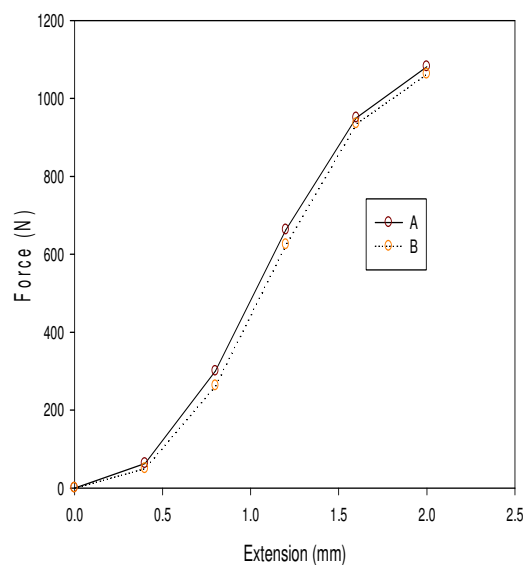


Fig. 3: Force against extension graph for the samples in 0.1M HCl.

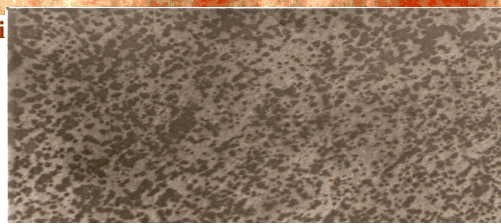


Plate 3: Micrograph of Sample A after 120h in 0.1M HCl

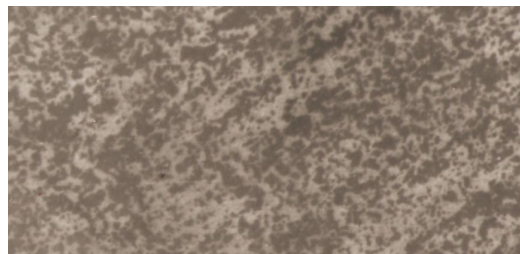


Plate 4: Micrograph of Sample A after 360h in 0.1M HCl



Plate 1: Micrograph of control Sample A

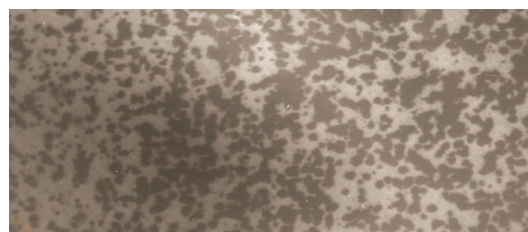


Plate 5: Micrograph of Sample A after 720h in 0.1M HCl



Plate 2: Micrograph of control Sample B

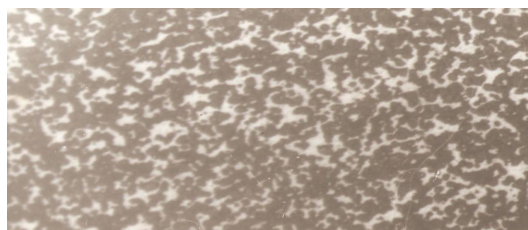


Plate 6: Micrograph of Sample A after 120h in sea water

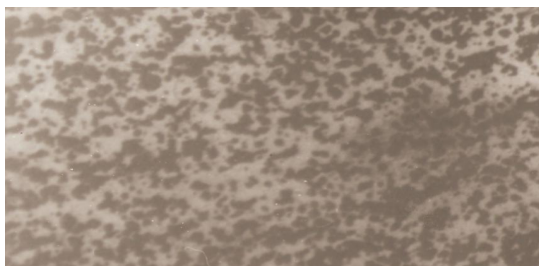




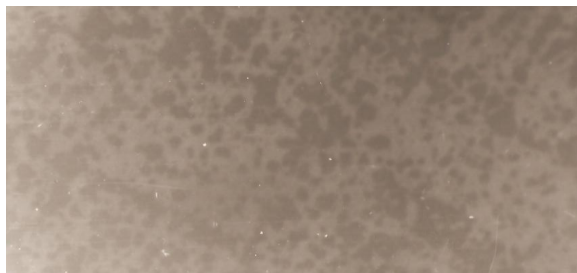
*Plate 7: Micrograph of Sample A after 360h in sea water*



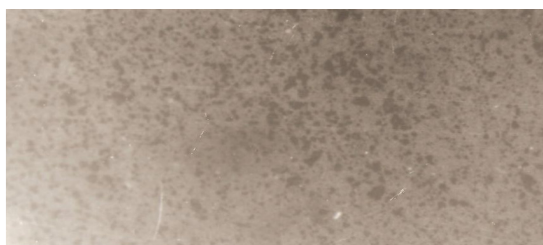
*Plate 11: Micrograph of Sample B after 720h in 0.1M HCl*



*Plate 8: Micrograph of Sample A after 720h in sea water*



*Plate 12: Micrograph of Sample B after 120h in sea water*



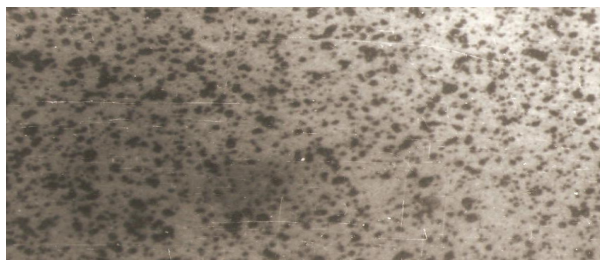
*Plate 9: Micrograph of Sample B after 120h in 0.1M HCl*



*Plate 13: Micrograph of Sample B after 360h in sea water*



*Plate 10: Micrograph of Sample B after 360h in 0.1M HCl*



*Plate 14: Micrograph of Sample B after 720h in sea water*