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The effect of zinc additions to the corrosion rates and tensile strengths of aluminium system

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Zinc oxide concentrations of 0.2778, 0.3012, 0.3821, 0.4942 and 0.5915 wt% were added to a standard mixture of the composition of an aluminum system. The systems were produced into rectangular flat sheet samples of about 5 mm thickness produced by First Aluminum Alloy Ltd, Port Harcourt, Nigeria. Ten coupon specimens (5 x 20 x 50 mm size) identified as A, B, C, D and E were polished, cleaned, washed in running warm-water and dried. Standard corrosion test technique was applied to the samples under different acidic concentrations. Likewise the tensile strengths of the system were measured before and after exposure to various media. The data obtained indicated a progressive increase and latter decrease of corrosion rates as exposure period increases. The tensile strengths decreased in the reverse order. Similarly corrosion rates increased relative to increasing exposure time except sample C (0.3821 wt%) that had a deviation from the trend. Generally results showed normal rate profile (for passivity of metals). There was an initial steep rise, then a progressive decline in all the media. This attack could be linked to increased grain boundary concentration arising from maximum solid solubility process.

Key words: Corrosion, zinc addition, aluminum, tensile strengths, acid media.

INTRODUCTION

Aluminum is extracted from its ores by expending a lot of energy and money. In pure state, its usefulness and applications are very limited. However by alloying, the physical and mechanical properties are improved for wider applications. Aluminum when formed quickly develops a thin protective oxide layer (Pourbair, 1974). The thickness of aluminum oxide formed depends on the temperature at which it was formed ranging from 2 - 3 nm at room temperature to 20 nm at about 450°C (Shimizu, 1991).

The service life of most engineering materials depends on its ability to resist degradation. This has created serious consequences which became a problem of word wide concern. Some metals are more intrinsically resistance to corrosion than others, due to the fundamental nature of the electrochemical processes involved or the behaviour of metals. Although some behaviours are generally governed by similar basic principles, most are not easily predictable under the continuous changing environmental conditions (Ijomah, 1991).

Aluminium and its alloys are widely used in services such as transportation, armory, and marine industries due to their high strength to weight ratio. They relatively resist corrosion when exposed to various aggressive environments. These environments may include water vapour, acid and base solutions (Pourbair, 1974). Most of these environments degrade the quality of the aluminum and its alloys and affects the mechanical properties of the system thereby reducing their life-span. For example, aggressive ions of sulphate, chloride, fluoride and other impurity elements such as tin and lead incorporated in the alloy may destabilize the alloy (Nisancioghi, 1992). Particularly sulphate species have been found to be most abundant indoor and outdoor constituents of the corrosion layers for aluminium products (Graedel, 1989).

This makes them unstable in certain environment that enhances their chemical combination with other elements in their environment to form stable compounds. On their

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return to their natural stable form of ground state known as ores an accompanying reduction in the free energy of the system occurs (Ezi et al., 2006). These structural defects could to a large extent be a major determinant of the degree of resistance of metal components to the effects of media-driven corrosion (Idenyi et al., 2004).

The adoption of good professional ethics in material selection must be adhered to right from the design, construction and the service stages (Ihom, 2004; Fontana, 1987).The destabilization of the aluminium system may manifest as pitting, intergranular, galvanic, localize, uniform corrosion (Nisancioghi, 1992). In these corrosion processes, an active phase may corrode preferentially (Calister, 1997).

Aluminium system was exposed to the atmosphere where Gaedel (1989) assessed that three chemical reaction processes were involved in removing the aluminum oxide layer: (i) high acidities to be responsible for supply of aluminium ions to the surface water by dissolving the oxide; (ii) as a result of chemical complexity, insoluble amorphous aluminium sulphate is favoured; (iii) chlorides are formed by replacement of hydroxidemoieties in the aluminium oxyhydroxide surface layer.

The corrosion penetration rate (CPR) or the rate of material removal is generally expressed in mils/years or mm/yr. This is an important corrosion monitoring index in terms of the degrees of corrosion process in a given material. The mathematical relation for CPR is given by:

$$CPR = \frac{kW}{\rho At} \qquad (1)$$

where W is weight loss after exposure time t, ρ and A are density and exposed surface specimen area respectively, and K is a constant whose magnitude depends on the system of unit. For instance, when K = 87.6, CPR is in mm/yr, and w, t, ρ and A are expressed in mg, h, g/cm^3 and cm^2 respectively (Callister, 1997). For most applications, a corrosion penetration rate of less than about 0.50mm/yr is acceptable (Uhlig, 1971). This estimation is suitable only for uniform corrosion (Landrum, 1990).

The selection of the appropriate material for a given engineering application in a given environment is very deterioration of their physio-mechanical properties by large number of diverse environments.

Despite the cost of high quality, a balance must be met between cost of frequent replacement/repairs and ab-initio use of high quality materials (Onuchukwu, 2004).

It is not always economically feasible to employ the material that offers the maximum corrosion resistance. Many a times, alteration in the concentration of some species in the medium produces a positive effect like passivation of the metal. Such alteration in the media concentration is generally achieved by the use of corro-

sion inhibitors, which when introduced normally in small quantities retards the corrosion process of the environment (Shreir, 1994). The inhibition is achieved by one or more of several mechanisms (Ijomah, 1991). More often than not if the target specimen is moved to a similar environment containing no inhibitors, the rate of attack returns to a high value (Shreir et al., 1994). In other situations, it may be more economical to choose the materials to suit the design (Chandler, 1985; Ihom, 2001).

Over time a judicious selection of materials once the environment has been characterized (Stachle, 1989) had been the best option. For instance, the passivity of some normally active metals and alloys under a given environmental condition may be reverted to active state by changing the characteristics of the environment. Such damage(s) to pre-existing passive film could result in a substantial increase in corrosion rate by as much as 10^5 (Callister, 1997).

The area relationship of the cathode and the anode must always be remembered in welds and other joints. That is, a small anode should not be connected to a large cathode as this amplifies corrosion rate (Wernick et al., 1987). Aluminium has a strong affinity for oxygen and environments habouring aluminium (and some of its alloys) assists in the formation of this passive surface film bonded strongly to its surface. This is stable in aqueous media where the pH is between 4.0 and 8.5.

This present work will consider the service performance of Al-Zn alloys in various concentrations of tetraoxosulphate. Also the mechanical properties before and after exposure will be examined. The outcome of the work would enable proper understanding of the corrosion behaviour of Al-Zn alloys when subjected to environments that are positively acidic due to acid rain generation.

MATERIALS AND METHOD

Five different zinc content compositions of 0.2778, 0.3012, 0.3821, 0.4912 and 0.5915 wt% in the form of zinc oxide were added to the normal standard composition of an aluminium roofing sheet system. The designed components systems were produced into rectangular flat sheets of about 5 mm thickness by First Aluminium Nigeria Limited, Port Harcourt, Nigeria. Ten coupons specimens (5 x 20 x 50 mm size) of each composition (identified as A, B, C, D and E depending on the amount of zinc oxide added) were polished to mirror finish, cleaned, washed in running warm water and then dried.

The environments for the work was purely acidic (environments with two different concentrations of tetraoxosulphate (vi) acid) The concentrations were 0.5 and 1.0 M of the acid solutions.

In each beaker containing the various concentrations of H_2SO_4 were suspended ten (10) samples each of the alloys. The set up was allowed to stand for 144 h (Figure 1). A set of coupons were withdrawn every 24 h and cleaned. The final weight of each of the test sample was determined.

The electronic digital weighing machine with model number x 21-0014 KERN770-15, 15467301 made in Germany with an accuracy of 0.0001 g was applied before and after exposure to the environment (media).
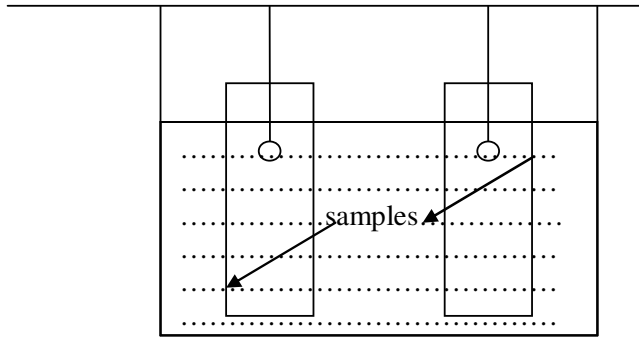
Figure 1. Sample set-ups for corrosion test.

Table 1. Corrosion rate variation data for sample A at different concentration of H_2SO_4.

Time (h)	Wt. Difference (g)	Corrosion rate (mm/yr)
24	0.0233	1.9870
48	0.0567	2.7689
72	0.0974	3.7684
96	0.1768	4.9590
120	0.2539	4.3304
144	0.3424	4.3560
1.0M H_2SO_4		
24	0.0426	3.6329
48	0.0981	4.1830
72	0.1718	4.8837
96	0.2359	5.0298
120	0.0582	1.6853
144	0.0605	0.8599

Mechanical tensile test

Standard test specimens were prepared with the test ends fixed into: a fixed-end and the other at loading-end of the measurement device. The device applied is the INSTRON Universal Tensile testing Machine, Model TT-DNL-A0674. All the specimens were tested in air at room temperature of 35^oC. The tests were conducted in the tensile loading mode at gauge length of 50 mm at a constant displacement speed of 200 mm/min. whereas specimens of 12.5 mm width, 50 mm length and thickness of 5 mm were applied and the mean extension tensile strength recorded.

RESULTS AND DISCUSSION

Using the weight loss values and equation (1), the corrosion rate profiles were calculated. Figures 1-6 represent the corrosion rate profiles against exposure time for the alloys in the different media concentrations. It was observed from the corrosion rates (Figures 1-6 and Tables 1-5) that samples A, B, D, and E show initial progressive increase and then a reduction in rates where as sample indicated continuous increase but latter fairly uniform
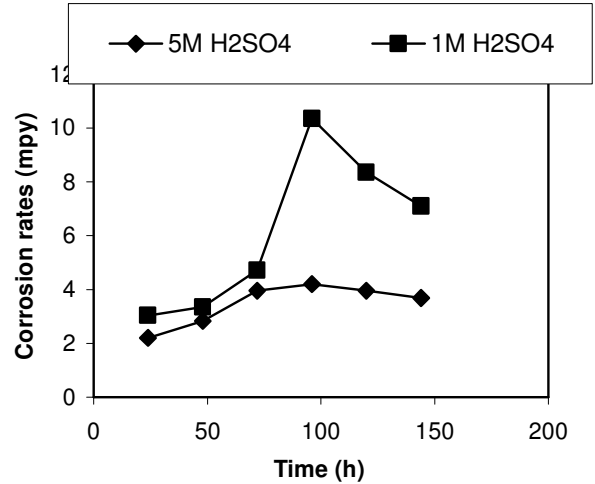

Figure 2. Variation of corrosion rates with exposure time for sample A.

Table 2. Corrosion rate variation data for Sample B at different concentration of H_2SO_4.

Time (h)	Wt. Difference (g)	Corrosion rate (mm/yr)
24	0.0258	2.1937
48	0.0667	2.8344
72	0.1398	3.9623
96	0.1972	4.1919
120	0.2312	3.9644
144	0.2595	3.6777
1.0M H_2SO_4		
24	0.0356	3.0270
48	0.0789	3.3543
72	0.1664	4.7162
96	0.4874	10.3606
120	0.4916	8.3600
144	0.5010	7.0998

crease in corrosion process. Generally, the specimens obeyed the rule of decrease of corrosion rates with increasing exposure time. This could be attributed to the partial development of passivity of the aluminium alloy at initiation of corrosion.

Tables 1-5 indicated trends of direct relationship between weight loss and concentration of the media as the range of increasing exposure time was maintained. The wt % losses increases with exposure time were maintained. The loss increased as a percentage of the reinforcing phase increased in the aluminium alloy system within the acidic environments. It equally showed normal corrosion rate profile for passivating metals subjected to stimulated environments. The trend showed initial rapid steep rise in corrosion rate corresponding to
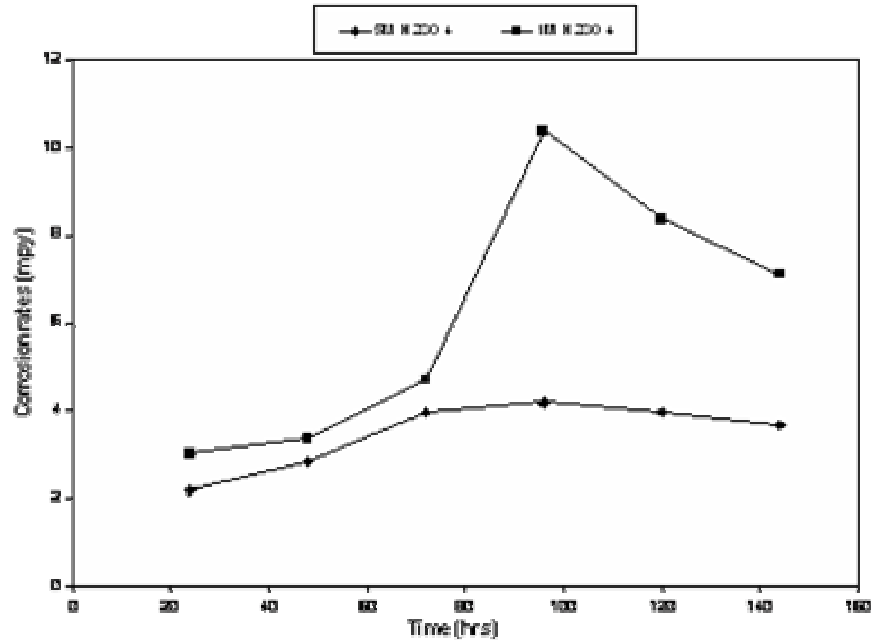
Figure 3. Variation of corrosion rates with exposure time for sample B.
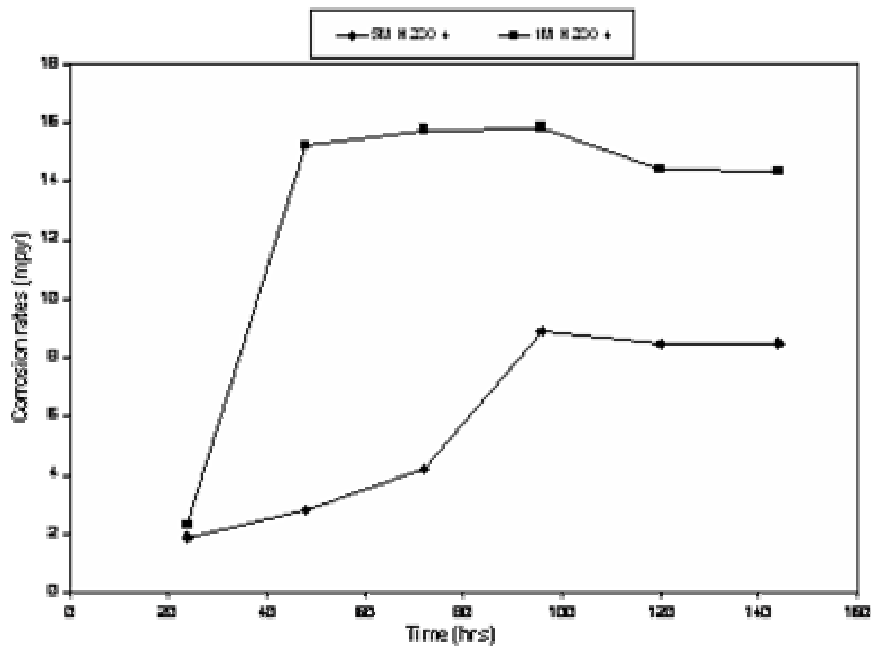

Figure 4. Variation of corrosion rates with exposure time for sample C.

the active region, until a maximum was attained. There-after the corrosion rates progressively decline with the time of exposure. This could be due to the adsorption of oxide film (alumina) on the metal surface. that created a barrier between the metal substrate and the environ-ment. Consequently, this reduced the corrosion rates.

This behaviour is in agreement with previous works, which suggest that, the initial steep rise in corrosion rate rate for the composites is thought to be due to increased mismatch between the matrix and the mechanism (Ogbonna et al., 2004). The seemingly exponential de-crease in corrosion rate is most probably due to immo-
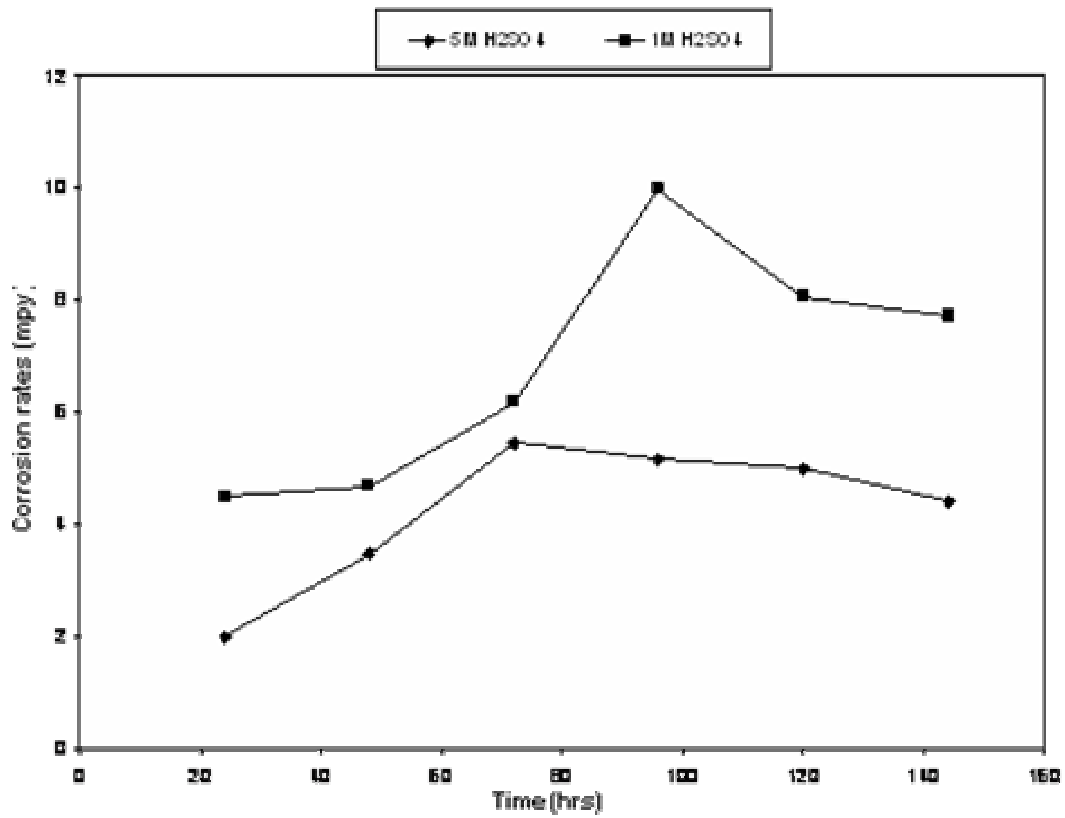
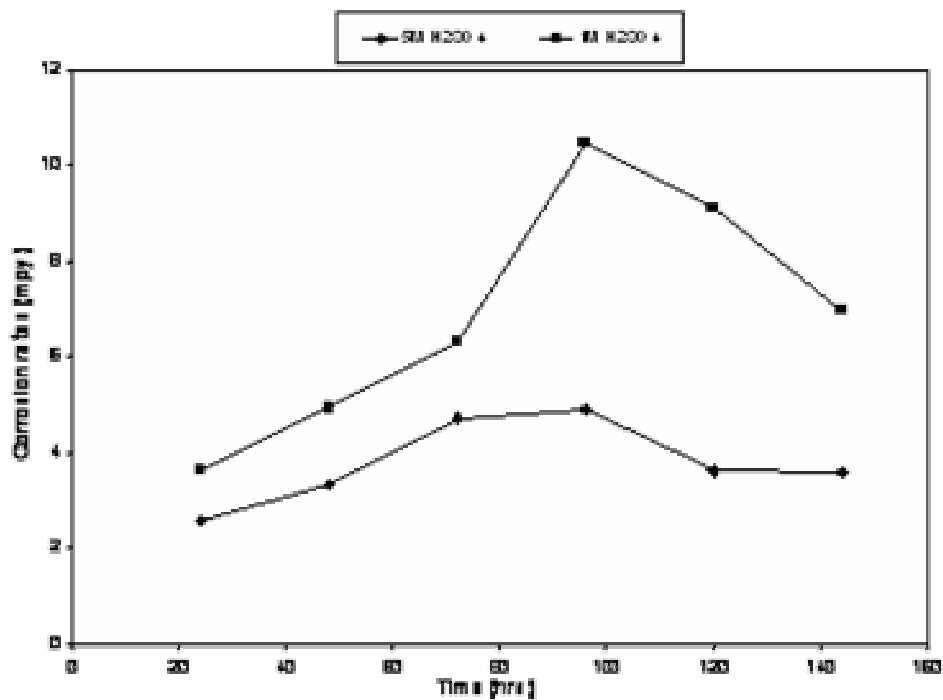**Figure 5.** Variation of corrosion rates with exposure time for sample D.

Figure 6. Variation of corrosion rates with exposure time for sample E.

Table 4. Corrosion rate data variation for Sample D at different various concentration of H_2SO_4.

Time (h)	Wt. Difference (g)	Corrosion rate (mm/yr)
24	0.0231	2.9775
48	0.0811	3.4722
72	0.1910	5.4503
96	0.2407	5.1507
120	0.2914	4.9887
144	0.3094	4.4144
1.0M H_2SO_4		
24	0.0524	4.4857
48	0.1093	4.6792
72	0.2168	6.1860
96	0.4660	9.9882
120	0.4711	8.0658
144	0.5409	7.7176

Table 5. Corrosion rate data variation for sample E at different concentration of H2SO4.

Time (h)	Wt. Difference (g)	Corrosion rate (mm/yr)
24	0.0309	2.5490
48	0.0804	3.3148
72	0.1714	4.7132
96	0.2375	4.8976
120	0.2184	3.6037
144	0.2603	3.5794
1.0M H2SO4		
24	0.0309	2.5490
24	0.0441	3.6380
48	0.1193	4.9194
72	0.2301	6.3273
96	0.5072	10.4602
120	0.5506	9.0844
144	0.5070	6.9693

bility of current carrying ions arising from saturation phenomenon attributable to the stability of the naturally naturally formed oxide film. However, a cursory look at the weight loss values showed that the initial increase with increasing exposure time peaked at an average of 96 h and then progressively declined as the exposure time increased. This trend is in conformity with existing theories suggesting that media saturation could be an important corrosion-monitoring index during passivation. In terms of alloy compositions, the Al 0.3821 wt% Zn alloy showed the highest values of weight loss and the most affected. This suggests that Sample C may well represent the maximum solid solubility of Zn in Al. This appears to correspond to maximum grain boundary concentrations. Hence, increased corrosion reaction to be

obsequious sites for corrosion attacks.

From the Tables 1-6 the normal corrosion rate profile for passivating metals subjected to corrosive environment was observed in all the media concentrations and for all the samples. There was an initial increase in corrosion rates corresponding to the active region reaching a peak value, after which due to adsorption of the formed oxide layer on the metal surface, the rate of corrosion progressively decline as a result of passivity. In comparative terms, sample C representing 0.3821 wt% Zn composition indicated highest values of corrosion penetration rate in virtually all the media concentration, especially in 1.0 M concentration. This correlates with the observation in weight loss values earlier discussed. The 0.382 wt% is believed to represent the maximum solid solubility (solvus line) of zinc in aluminium meaning that maximum grain boundary concentration existed in this alloy thus promoting corrosion reactions in this case. As expected (Table 6) the tensile strength indicated gradual reduction in the mechanical strengths of the materials when compared with equivalent exposure to controlled open air environment. For example, mean reduction in strengths by 9.61% in 0.5 M H_2SO_4 and 19.93% in 1 M H_2SO_4 were determined. These values are considered acceptable when compared with the very fact that the drastic and harsh acidic test environments are hardly attainable in practice. Comparatively, sample C had the lowest percentage decrease in tensile strengths.

Conclusion

The analyses have shown that though pure aluminium is considered highly corrosion resistant in diverse environments (pH 4.0 to pH 8.5) due to the phenomenon of passivation. The presence of alloying elements (in this case zinc), which acts as impurity can and indeed reduce environments. In our case, it is believed that the degreeto which it resists corrosion in the stimulated presence of zinc in aluminium makes it more prone to corrosion attack due to the formation of possible zinc-rich phase. The eutectic compounds could create micro-galvanic cells within the matrix, causing flaws on the alloy surface, hence creating pits and inter and trans-granular cracking. This is occasioned by bimetallic corrosion and selective dissolution which is a well-known problem in most binary alloy systems in aqueous media. Based on the foregoing discussions, it is concluded that passivation phenomenon is a consequence of both alloy impurity atom concentration and media molarity. The observed severity of attack on the 0.382 wt% Zn alloy is attributed to possible maximum solubility of zinc in aluminium within this range.

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Table 6. Tensile strength variation before and after exposure to acidic media.

Sample	Open air controlled environment	Elongation (%)	0.5M H_2SO_4	Reduction (%)	Elongation (%)	1M H_2SO_4	Reduction (%)	Elongation (%)
A	272.81	6.34	245.53	9.99	7.40	212.0	22.29	8.12
B	249.47	3.50	212.05	14.99	4.14	195.2	21.75	5.32
C	108.64	2.4	257.18	10.89	3.80	241.5	16.33	4.34
D	269.98	4.4	241.63	10.50	5.71	216.5	19.81	6.20
E	260.62	2.6	232.74	10.69	4.01	209.8	19.49	4.84

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