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## The Effects of Zinc Additions on the Corrosion Susceptibility of Aluminium Alloys in Various Tetraoxosulphate (VI) Acid Environments

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**Abstract:** The influence of zinc additions on the corrosion behaviour of aluminium alloys in  $H_2SO_4$  solution of varying concentrations has been investigated. Aluminium-zinc alloys of 1.0, 2.0, 2.5, 3.5 and 4.0% zinc by weight were cast and machined to cuboidal test coupons of initial surface area averaging  $12.71 \text{ cm}^2$ . The coupons were then weighed and immersed into beakers containing 0.5 M and 1.0 M  $H_2SO_4$  solutions. The set-ups were allowed to stand for six days with a set withdrawn daily for corrosion rate characterization using standard procedures. The results showed that although, the normal corrosion rate profile (for passivating metals) of an initial steep rise, then a progressive decline was observed in all the media as the fraction of the solute in the alloy increased, there was severity of attack on the 2.5% Zn alloy. It is concluded that the severity of attack on the 2.5% Zn alloy is due to increased grain boundary concentration possibly implying a maximum solid solubility (solvus line) in Al-Zn binary systems within this range.

**Key words:** Corrosion, aluminium, zinc, solvus line, passivation, grain boundary

### INTRODUCTION

The service life of most engineering materials depend on their ability to resist degradation. Some metals are more intrinsically resistance to corrosion than others, either due to the fundamental nature of the electrochemical processes involved or due to the details of how reaction products form. Corrosion behaviour of metals although, generally governed by the same basic principle is not always predictable under the countless and changing environmental conditions of their uses (Ekuma and Idenyi, 2006).

The main factor that causes corrosion of metals is the consequence of their temporal existence in a state of higher energy level due to the absorbed energy during extraction from their ores. This makes them unstable and certain environments enhance their combination chemically with elements in their environment to form compounds and return to their natural stable ore state with accompanying reduction in the free energy of the system (Ekuma and Idenyi, 2006).

It must be asserted that corrosion resistant alloys or sophisticated surface treatment is of little use if parts are designed without the utilization of some basic corrosion knowledge. It will also be the cheapest and the best if potential corrosion cases can be eliminated at the design stage instead of dealing with the symptoms of bad design afterwards. Hence, the adoption of good professional

ethics in material selection must be adhered to right at the design stage, construction stage and the service stage (Ihom, 2004), i.e., to design-out corrosion out of the equipment (Fontana, 1987).

The Corrosion Penetration Rate (CPR) or the rate of material removal as the consequence of the physicochemical interactions mostly expressed in mils/year or  $\text{mm year}^{-1}$  is an important corrosion-monitoring index that gives reliable information to corrosion experts on the degree of corrosion progress in a given material in service. The mathematical computation of CPR is based on the formula

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

Where, W is weight loss after exposure time t,  $\rho$  and A are density and exposed specimen area respectively and K is a constant whose magnitude depends on the system of units used. For instance, when  $K = 87.6$ , CPR is in  $\text{mm year}^{-1}$  and w, t,  $\rho$  and A are expressed in mg, h,  $\text{g cm}^{-3}$  and  $\text{cm}^2$  respectively (Idenyi and Ekuma, 2006). For most applications, a corrosion penetration rate of less than about 0.50 mm year is acceptable (Ekuma and Idenyi, 2006). However, this estimation is suitable only for uniform corrosion and becomes somewhat erratic with local instability (Idenyi *et al.*, 2006).

It is not always economically feasible to employ the material that offers the maximum corrosion resistance and as such, most times, either another alloy and/or some other measures must be employed. 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 corrosion inhibitors, which when introduced normally in small quantities retards the corrosiveness of the environment (Idenyi *et al.*, 2004). The inhibition is achieved by one or more of several mechanisms. Some inhibitors retard corrosion by adsorption of an invisible thin film or, perhaps, visibly bulky precipitates on the metal surface (Ijomah, 1991). More often than not, the corrosion retardation effect of inhibitors only continue so long as the inhibitor is present and if the target specimen is moved to a similar environment containing no inhibitors, the rate of attack returns to a high value (Callister, 1997). In other situations, it may be more economical to choose the material to suit the design (Chandler, 1985) which is a sensible approach provided it is part of the design philosophy (Ihom, 2004).

The strength of all engineering materials depends mainly upon the extent environments influence their reactivity and subsequent degradation of these materials has been attributed to this. In order to define the strength of an engineering material for a corrosion based design, it is essential to first define the nature of the environment affecting the material over time to enable a judicious selection of materials once the environment has been characterised (Staehle, 1989). For instance, the passivity of some normally active metals and alloys under a given environmental condition where they lose their chemical reactivity and become immune to corrosion attack may be reverted to active state by change in the character of the environment. Such damage (s) to pre-existing passive film could result in a substantial increase in corrosion rate by as much as  $10^5$  (Ekuma and Idenyi, 2006).

Aluminum owes its excellent corrosion resistance and its usage as one of the primary metals of commerce to the barrier oxide film-alumina ( $Al_2O_3$ ). Aluminium has a strong affinity for oxygen and in environments harbouring aluminium (and some of its alloys), assists in the formation of this passive surface film bonded strongly to its surface, which is stable in aqueous media when the pH is between about 4.0 and 8.5 and if damaged, re-forms immediately in most environments.

This present research aims at investigating the service performance of Al-Zn alloys in various concentrations of tetraoxosulphate (vi) acid. The outcome of this study would ensure proper understanding of the

corrosion behaviour of Al-Zn alloys when subjected to environments that are positively acidic and hence in material selection during the design of engineering systems.

## MATERIALS AND METHODS

**Materials/equipment:** The study of effect of zinc addition on the corrosion susceptibility of Al-Zn alloy systems was carried out in Abakaliki, Ebonyi State, Nigeria between October and November 2005.

The materials used for this research were scraps of aluminium (99% pure Al) purchased from aluminum stockist and pure granulated zinc metal procured also from metal stockist. The other materials used were: acetone, sodium chloride, distilled water, laboratory beakers, measuring cylinders, etc.

The equipments used were: lathe machine, drilling machine and a surface crucible furnace. The basic equipment used was analytic digital weighing machine X21-0014 KERN 770-15,15402301 made in Germany, which measures to an accuracy of 0.0001 g and it is used to weigh the sample coupons before and after immersion to know the exact weight difference.

**Sample preparation:** After the calculation for each of the Al-Zn alloy compositions have been carefully worked out and charged into the surface crucible furnace, the molten alloys were cast into rods after melt down, machined to sizeable dimensions and subsequently, cut into coupon samples of dimension range of  $17 \times 16.8 \times 15$  mm and initial surface area of about  $12.71 \text{ cm}^2$ . Each sample coupon was drilled with a 5 mm drill bit to provide holes for the suspension of the strings. The surface of each of the coupon specimen was thoroughly polished with emery clothes of 500, 1000 and 1200 m grades as to remove any oxide layers, carbonized layer and any initial treatment (s) given to the Al-Zn alloy as to expose of its structure for immersion.

The samples for 1% Zn-99% Al alloy were coded A; 2% Zn-98% Al alloy were coded B; 2.5% Zn-97.5% Al alloy were coded C; 3.5% Zn-96.5% Al alloy were coded D and 4% Zn-96% Al alloy were coded E. The initial weight of each of the sample coupon was taken using a highly sensitive digital analytic chemical weighing machine, which measures to an accuracy of 0.0001 g.

**Simulation of environment:** The environments for this work were acidic environments with two different concentrations made from tetraoxosulphate (vi) acid using normal procedure. The concentrations were 0.5 and 1.0 M of the acid solutions.

**Experimentation:** In each beaker containing the various concentrations of H<sub>2</sub>SO<sub>4</sub> were suspended six samples each of the alloys and the set up allowed to stand for 144 h. A set of coupon was withdrawn 24 h, washed with distilled water, cleaned with acetone and dried in an open air. The final weight of each of the test sample was determined using the digital analytic weighing balance.

**RESULTS AND DISCUSSION**

Table 1-5 represent the corrosion rate profile against exposure time for the alloys in the different media concentrations.

**Weight loss measurements:** From Table 1-5, it can be seen that the trend of direct relationship existing between weight loss and concentration of the media over the range of increasing exposure time was maintained. The loss increased as the percentage of the solute increased in the aluminium alloy system. It showed normal corrosion rate profile for passivating metals subjected to stimulated environments, which aluminium is known to belong. The trend showed initial rapid and steep rise in corrosion rate

Table 1: Corrosion rate data for Al-1.0% Zn in various concentrations of H<sub>2</sub>SO<sub>4</sub>

Time (h)	Initial wt. (g)	Final wt. (g)	Wt. difference (g)	Corrosion rate (mm year <sup>-1</sup> )
5 M H <sub>2</sub> SO <sub>4</sub>				
24	11.5072	11.4839	0.0233	1.9870
48	12.3342	12.2775	0.0567	2.7689
72	11.6420	11.5446	0.0974	3.7684
96	12.7023	12.5255	0.1768	4.9590
120	11.1824	10.9285	0.2539	4.3304
144	10.6664	10.3240	0.3424	4.1560
1.0 M H <sub>2</sub> SO <sub>4</sub>				
24	11.1339	11.0913	0.0426	3.6329
48	10.9551	10.8570	0.0981	4.1830
72	10.8097	10.6379	0.1718	4.8837
96	11.8194	11.5835	0.2359	5.0298
120	11.5237	11.0345	0.0582	1.6853
144	11.0868	11.0263	0.0605	0.8599

Table 2: Corrosion rate data for Al-2.0% Zn in various concentrations of H<sub>2</sub>SO<sub>4</sub>

Time (h)	Initial wt. (g)	Final wt. (g)	Wt. difference (g)	Corrosion rate (mm year <sup>-1</sup> )
0.5 M H <sub>2</sub> SO <sub>4</sub>				
24	11.7813	11.7555	0.0258	2.1937
48	10.2492	10.1825	0.0667	2.8344
72	11.8927	11.7529	0.1398	3.9623
96	10.7773	10.5801	0.1972	4.1919
120	11.2290	10.9978	0.2312	3.9644
144	12.3762	12.1167	0.2595	3.6777
1.0 M H <sub>2</sub> SO <sub>4</sub>				
24	10.8097	10.7741	0.0356	3.0270
48	10.7835	10.7046	0.0789	3.3543
72	11.3876	11.2212	0.1664	4.7162
96	12.0441	11.5567	0.4874	10.3606
120	11.3105	10.8189	0.4916	8.3600
144	12.1810	11.6800	0.5010	7.0998

Table 3: Corrosion rate data for Al-2.5% Zn in various concentrations of H<sub>2</sub>SO<sub>4</sub>

Time (h)	Initial wt. (g)	Final wt. (g)	Wt. difference (g)	Corrosion rate (mm year <sup>-1</sup> )
0.5 M H <sub>2</sub> SO <sub>4</sub>				
24	11.4200	11.3977	0.0223	1.8772
48	11.1753	11.1089	0.0664	2.7940
72	10.3522	10.2024	0.1498	4.2043
96	11.5852	11.1862	0.3990	8.3970
120	11.5320	11.1239	0.4081	6.8711
144	11.9535	11.4768	0.4767	6.6880
1.0 M H <sub>2</sub> SO <sub>4</sub>				
24	11.8409	11.7903	0.0506	2.2595
48	10.9513	10.5894	0.3619	15.2323
72	11.9976	11.4363	0.5613	15.7510
96	10.7562	10.0039	0.7523	15.8315
120	10.9394	10.0854	0.8540	14.3776
144	10.9191	10.0400	0.8791	12.3343

Table 4: Corrosion rate data for Al-3.5% Zn in various concentrations of H<sub>2</sub>SO<sub>4</sub>

Time (h)	Initial wt. (g)	Final wt. (g)	Wt. difference (g)	Corrosion rate (mm year <sup>-1</sup> )
0.5 M H <sub>2</sub> SO <sub>4</sub>				
24	11.7055	11.6824	0.0231	1.9775
48	9.9627	9.8816	0.0811	3.4722
72	10.8050	10.6140	0.1910	5.4503
96	11.9043	11.6636	0.2407	5.1507
120	10.3213	10.0299	0.2914	4.9887
144	9.9155	9.6061	0.3094	4.4144
1.0 M H <sub>2</sub> SO <sub>4</sub>				
24	11.2755	11.2231	0.0524	4.4857
48	11.1700	11.1662	0.1093	4.6792
72	10.3778	10.1610	0.2168	6.1860
96	10.8313	10.3653	0.4660	9.9882
120	11.8102	11.3391	0.4711	8.0658
144	10.1293	9.5884	0.5409	7.7176

Table 5: Corrosion rate data for Al-4.0% Zn in various concentrations of H<sub>2</sub>SO<sub>4</sub>

Time (h)	Initial wt. (g)	Final wt. (g)	Wt. difference (g)	Corrosion rate (mm year <sup>-1</sup> )
0.5 M H <sub>2</sub> SO <sub>4</sub>				
24	9.9874	9.9565	0.0309	2.5490
48	10.5386	10.4582	0.0804	3.3148
72	9.5087	9.3373	0.1714	4.7132
96	10.0906	9.8531	0.2375	4.8976
120	9.2729	9.0545	0.2184	3.6037
144	10.8240	10.5637	0.2603	3.5794
1.0 M H <sub>2</sub> SO <sub>4</sub>				
24	9.1458	9.1017	0.0441	3.6380
48	9.3250	9.2057	0.1193	4.9194
72	9.9231	9.6930	0.2301	6.3273
96	9.4459	8.9387	0.5072	10.4602
120	9.0317	8.4811	0.5506	9.0844
144	10.1522	9.6452	0.5070	6.9693

corresponding to the active region, until a maximum is attained after which, the corrosion rate progressively declined with the time of exposure. This is due to the adsorption of the formed oxide film (alumina) on the metal surface creating a barrier between the metal substrate and the environment consequently, reducing the corrosion rate; a phenomenon referred to as passivation. This behaviour is in agreement with previous works, which suggests that, the initial steep rise in corrosion rate for the

alloys is thought to be due to increased mismatch between the matrix and the mechanisms: bimetallic corrosion and possibly crevice attack and pitting corrosion (Ekuma and Idenyi, 2006). The somewhat exponential decrease in corrosion rate is most probably due to immobility of current carrying ions as a result of saturation phenomenon attributed to the stability of the 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 exposure time before progressively declining 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 since the rate of deposition would be hindered by ion mobility, which is generally low for extremely saturated media. In terms of alloy compositions, the Al-2.5% Zn alloy showed the highest values of weight loss and therefore, the most affected with heavy pitting. This suggests that the 2.5% Zn may well represent the maximum solid solubility of Zn in Al; corresponding to maximum grain boundary concentrations. Hence, increased corrosion reaction kinetics is expected since grain boundaries are known to be obsequious sites for corrosion attacks.

**Corrosion rate profile:** From the results, the normal corrosion rate profile for passivating metals subjected to corrosive environment was observed in all the media concentrations and for all the alloy samples. There was an initial increase in corrosion rate 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 declined as a result of passivity. In comparative terms, sample C representing 2.5% Zn weight composition also showed the 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 2.5% Zn 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.

### CONCLUSIONS

The analyses have shown that though pure aluminium is considered highly corrosion resistant in diverse environments (pH 4.0 to 8.5) due to the phenomenon of passivation, the presence of alloying elements (in this case zinc), which acts as impurity can

and indeed does reduce the degree to which it resists corrosion in the stimulated environments. In our case, it is believed that the presence of zinc in aluminium makes it more prone to corrosion attack due to the formation of a zinc-rich phase ( $Zn_3Al$ ). This eutectic compound creates micro-galvanic cells within the matrix, causing flaws on the alloy surface, hence creating pits and inter-or trans-granular cracking 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. In this particular study, the observed severity of attack on the 2.5% Zn alloy is attributed to possible maximum solubility of zinc in aluminium within this range.

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