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The Inhibition Characteristics of Brine on the Corrosion Susceptibility of Al-Zn Alloy Systems

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Abstract: The effects of zinc additions on the corrosion susceptibility of aluminium alloys in varying concentrations of NaCl solution have been studied. Virgin aluminium alloys containing 1.0, 2.0, 2.5, 3.5 and 4.0% Zn by weight were cast and machined into cylindrical coupons of average surface area of 12.71 cm^2. The initial weights of the coupons were determined and immersed in beakers containing 0.1, 0.25, 0.5 and 1.0 M NaCl solution. The set-ups were allowed to stand for six days with a set withdrawn 24 h for corrosion rate determination using standard procedures. The results showed that although the normal corrosion rate profile (for passivating metals) was observed as the reinforcing phase increased, the samples gained weight; indicating an all-through passivation, especially in the 2.5% Zn alloy. It is concluded that the passivation is a consequence of media supersaturation and preferential oxide (Al_2O_3) adsorption on the metal surface and that the 2.5% Zn composition may well represent the solvus line in Al -Zn binary systems.

Key words: Corrosion, aluminium, zinc, adsorption, solvus line, passivation, supersaturation

INTRODUCTION

The service life of most engineering materials depends on their ability to resist degradation, whose serious consequences have become a problem of worldwide concern. 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 (Ijomah, 1991).

Corrosion, derived from the Latin word corrosus meaning gnawed away, occurs as a result of a physicochemical interaction between the material, mostly a metal and its environment. As a result, the mechanical properties of metals may be greatly impaired even when no visible change is observed on the surface of the metal (Wranglen, 1985). Factors that define corrosive environment include moisture content, air permeability (porosity), salinity (and salt analysis), acidity, alkalinity, conductivity and presence of micro-organisms (Asoegwu and Ogbonna, 2000).

Material selection for engineering applications has been hampered by the deterioration of their physio-mechanical properties by large number of diverse environments; even with the wide range of engineering materials modern technology has at its disposal. This makes material selection for a given application of prime importance. However, no general rule governs this choice, but a logical decision normally involves a consideration of those properties that are to be preserved in any environment (Onuchukwu, 2004).

The main factor that causes corrosion of metals is the consequence of their temporal existence in a state of higher energy level; a refined state due to the absorbed energy during extraction from their ores. This makes them unstable and certain environments offer the opportunities for these metals (or alloys) to combine chemically with elements in them to form compounds and return to their natural stable form of ground state known as ores with accompanying reduction in the free energy of the system. Also, metal (or alloy) deform principally due to the motion of existing dislocations coupled with the interaction of many additional dislocations in a crystallographic unit cell. 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 Corrosion Penetration Rate (CPR) or the rate of material removal as the consequence of the physicochemical interactions usually expressed mainly in mils/year or mm/year is an important corrosion-monitoring index. It gives reliable information to corrosion experts on the extent of corrosion progress in a given material in service. The mathematical computation of CPR is based on the formula:

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

Corresponding Author: C.E. Ekuma, Department of Industrial Physics, Ebonyi State University, P.M.B. 053, Abakaliki, Nigeria where W is weight loss after exposure time t, ρ 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 mm/year 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 0.50 mm year is acceptable (Uhlig, 1971). However, this estimation is suitable only for uniform corrosion and becomes somewhat unreliable with local disturbances (Landrum, 1990). The corrosion rate can also be estimated from the weight gain of materials in service environment. Inasmuch as the oxide scale reaction product normally adsorbed permanently on the material surface, the corrosion penetration rate (rate of reaction) can be determined by measuring the weight gain per unit area as a function of time (Callister, 1997). The weight difference Δ W can then be substituted in the CPR formula to get the corrosion rate profile.

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 (Callister, 1997).

For a passivated film to be effective, it must provide a protective barrier that keeps the corrosion current on the metallic surface at a low enough rate so that the extent of corrosion damage is minimized. An effective film is one that resists the breakdown of the passive film (Frankenthal and Kruger, 1978). It should be noted that all breakdown mechanisms involve a damaging species. Unfortunately, one of the major damaging species causing breakdown of passivity is the aggressive chloride ion, which is abundantly available in nature. Passivation phenomena are better studied in terms of polarization potential log-current density curves for which the shapes for passivating metals are readily available (Schweitzer, 1989).

Aluminum owes its excellent corrosion resistance and its usage as one of the primary metals of commerce to the barrier oxide film -the alumina (Al_2O_3). Aluminium has a strong affinity for oxygen and in environments habouring 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 notwithstanding, aluminium alloys, especially those containing zinc, magnesium, manganese, etc., are known to manifest reduced corrosion resistances in acidic and alkaline environments. Ijomah (1991), had suggested that saline environments as close to the concentration of sea water are known to exhibit passivation characteristics for aluminium-base alloys.

This present study aims at investigating the service performance of Al-Zn alloys in various concentrations of brine, which contains the aggressive chloride ion (Cl^-). This is of practical importance because, it is present in large amount both in sea water, road salts and some soils and in lower concentration in other natural sources. The outcome of this study would ensure proper understanding of the corrosion behaviour of Al-Zn alloys when subjected to environments that are positively saline 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 September and October 2005.

The materials used for this work 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 X21-0014KERN770-15,15402301 made in Germany, which measures to an accuracy of 0.0001 g and it was 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 a surface crucible furnace, the molten alloys were cast into rods after melt down, machined to sizeable dimensions and subsequently, cut into test coupons of dimension range of 17×16.8×15 mm and initial surface area of about 12.71 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, 1200 and 2400 m grades as to remove any oxide layers, carbonized layer and any initial treatment(s) given to the Al-Zn alloy so as to expose 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 alkaline environments with four different concentrations made from sodium chloride salt using normal procedure. The concentrations were 0.10, 0.25, 0.5 and 1.0 M for the saline solutions.

Experimentation: In each beaker containing the various concentrations of NaCl were suspended six (6) samples of 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 coupon was determined using the digital analytic weighing balance.

RESULTS AND DISCUSSION

The results of the weight difference and the corrosion rate data of the test coupons immersed in the four test environments for the different time intervals of 1-6 days (set of coupons withdrawn 24 h for six days) were as shown in Table 1-5.

Weight loss measurements: All through the tables, it is observed that the alloys presented final weights greater than the initial weights over the periods of the study. Consequently, the weight differences were all positive, showing weight gains; thus indicating the phenomenon of passivation. However, a cursory look at the weight difference values shows an initial increase with increasing exposure time, peaking at an average of 96 h exposure time before progressively decreasing 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 highly saturated media. In terms of alloy compositions, the Al-2.5% Zn alloy showed the greatest values of weight gains and therefore, the most passivated and by extension, the most affected. 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 favourable sites for corrosion attacks.

Table 1: Corrosion rate data for Al- 1.0% Zn in various concentrations of NaCl

Time (h)	Initial wt. (g)	Final wt. (g)	Wt. difference (g)	Corrosion rate (mm/year)
0.1 M NaCl				
24	5.1122	5.1131	0.0009	0.0958
48	5.7118	5.7137	0.0019	0.1010
72	5.4792	5.4824	0.0032	0.1135
96	5.3206	5.3254	0.0048	0.1276
120	5.8201	5.8240	0.0039	0.0830
144	5.2868	5.2896	0.0028	0.0496
0.25 M NaCl				
24	4.1932	4.1947	0.0015	0.1595
48	4.1277	4.1307	0.0030	0.1595
72	4.0279	4.0318	0.0039	0.1382
96	4.8121	4.8167	0.0046	0.1223
120	4.3219	4.3257	0.0038	0.0809
144	4.9828	4.9858	0.0030	0.0532
0.5 M NaCl				
24	11.3816	11.3854	0.0038	0.4041
48	10.0660	10.0699	0.0039	0.2074
72	10.6266	10.6310	0.0044	0.1560
96	11.5720	11.5778	0.0051	0.1356
120	11.0785	11.0820	0.0035	0.0745
144	10.8741	10.8766	0.0025	0.0443
1.0 M NaCl				
24	11.1031	11.1067	0.0036	0.3829
48	12.1178	12.1220	0.0042	0.2234
72	10.1103	10.1126	0.0023	0.0815
96	10.3511	10.3527	0.0016	0.0425
120	11.6436	11.6446	0.0010	0.0213
144	11.2893	11.2902	0.0009	0.0160

Corrosion rate profile: From the tables, the normal corrosion rate profile for passivating metals was observed in all the media concentrations and for all the alloy samples. There was a progressive increase in corrosion (passivation) rate peaking at an average of 24 h of exposure time before decreasing with time. This implies that the rate of ion adsorption on the metal surface was high within the first 24 h but as ion migration to the metal surface increased, the passivation rate (in this context, the rate of deposition) decreased as a result of competition for the available surface among the ions. 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 0.25 M concentration (which is near the concentration of

Table 2: Corrosion rate data for Al- 2.0% Zn in various concentrations of NaCl

Time (h)	Initial wt. (g)	Final wt. (g)	Wt. difference (g)	Corrosion rate (mm/year)
0.1 M NaCl				
24	5.3291	5.3319	0.0028	0.2978
48	5.9882	5.9940	0.0058	0.2265
72	5.5467	5.5521	0.0054	0.1914
96	5.7059	5.7064	0.0050	0.1329
120	5.3216	5.3251	0.0035	0.0745
144	5.2504	5.2524	0.0020	0.0354
0.25 M NaCl				
24	6.3210	6.3238	0.0028	0.2978
48	6.6214	6.6268	0.0054	0.2872
72	6.7249	6.7286	0.0037	0.1312
96	6.3498	6.3518	0.0020	0.0532
120	6.3389	6.3408	0.0019	0.0404
144	6.0456	6.0472	0.0016	0.0284
0.5 M NaCl				
24	10.6605	10.6619	0.0014	0.1489
48	11.0855	11.0875	0.0020	0.1063
72	11.5419	11.5447	0.0028	0.0993
96	11.3575	11.3588	0.0013	0.0346
120	11.3534	10.3541	0.0007	0.0149
144	10.8392	10.8400	0.0008	0.0142
1.0 M NaCl				
24	10.0796	10.0857	0.0061	0.6488
48	11.3899	11.4003	0.0104	0.5530
72	10.7511	10.7658	0.0147	0.5212
96	11.3575	11.3688	0.0113	0.3005
120	11.3389	11.3464	0.0075	0.1595
144	12.3404	12.3479	0.0075	0.1329

Table 3: Corrosion rate data for Al- 2.5% Zn in various concentrations of NaCl

Time (h)	Initial wt. (g)	Final wt. (g)	Wt. difference (g)	Corrosion rate (mm/year)
0.1 M NaCl				
24	3.2117	3.2159	0.0042	0.4467
48	3.6474	3.6550	0.0076	0.4042
72	4.2189	4.2281	0.0092	0.3261
96	4.4844	4.4950	0.0106	0.2819
120	4.3200	4.3296	0.0096	0.2042
144	4.6516	4.6605	0.0089	0.1578
0.25 M NaCl				
24	4.7326	4.7385	0.0059	0.6275
48	4.6498	4.6621	0.0123	0.6541
72	4.2111	4.2236	0.0125	0.4432
96	4.2637	4.2772	0.0135	0.3589
120	4.3267	4.3390	0.0123	0.2617
144	4.0579	4.0687	0.0108	0.1914
0.5 M NaCl				
24	10.3873	10.3891	0.0018	0.2252
48	10.5333	10.5356	0.0023	0.1223
72	11.6740	11.6712	0.0028	0.0993
96	10.8624	10.8660	0.0036	0.0957
120	12.0010	12.0050	0.0040	0.0851
144	10.3078	10.3116	0.0038	0.0674
1.0 M NaCl				
24	10.3476	10.3487	0.0011	0.1170
48	10.8697	10.8717	0.0020	0.1064
72	11.9700	11.9728	0.0028	0.0993
96	11.0017	11.0054	0.0037	0.0984
120	10.1285	10.1323	0.0038	0.0807
144	11.6478	11.6522	0.0044	0.0780

Table 4: Corrosion rate data for Al- 3.5% Zn in various concentrations of NaCl

Time (h)	Initial wt. (g)	Final wt. (g)	Wt. difference (g)	Corrosion rate (mm/year)
0.1 M NaCl				
24	5.2188	5.2206	0.0018	0.1914
48	5.8279	5.8312	0.0033	0.1755
72	5.7576	5.7617	0.0041	0.1454
96	5.8506	5.8552	0.0046	0.1223
120	5.3856	5.3898	0.0042	0.0893
144	5.5735	5.5767	0.0032	0.0567
0.25 M NaCl				
24	7.2384	7.2412	0.0028	0.2978
48	7.0744	7.0798	0.0054	0.2872
72	7.0891	7.0955	0.0064	0.2269
96	7.0900	7.0971	0.0071	0.1897
120	7.3211	7.3263	0.0047	0.1000
144	7.4540	7.4668	0.0028	0.0496
0.5 M NaCl				
24	10.9866	10.9895	0.0029	0.3084
48	11.2445	11.2486	0.0041	0.2180
72	11.2391	11.2444	0.0053	0.1879
96	11.3171	11.3236	0.0065	0.1728
120	11.2307	11.2387	0.0080	0.1701
144	10.3814	10.3889	0.0075	0.1330
1.0 M NaCl				
24	11.1513	11.1539	0.0026	0.2765
48	10.6658	10.6696	0.0038	0.2021
72	10.1136	10.1184	0.0048	0.1702
96	11.6010	11.6052	0.0042	0.1116
120	10.4015	10.4055	0.0040	0.0850
144	11.2121	11.2155	0.0034	0.0603

Table 5: Corrosion rate data for Al- 4.0% Zn in various concentrations of NaCl

Time (h)	Initial wt. (g)	Final wt. (g)	Wt. difference (g)	Corrosion rate (mm/year)
0.1 M NaCl				
24	3.1127	3.1131	0.0004	0.0425
48	3.9933	3.9948	0.0015	0.0798
72	3.8782	3.8804	0.0022	0.0780
96	3.6381	3.6407	0.0026	0.0691
120	3.4789	3.4812	0.0023	0.0489
144	3.5118	3.5139	0.0021	0.0372
0.25 M NaCl				
24	4.6247	4.6255	0.0008	0.0851
48	4.6313	4.6332	0.0019	0.1010
72	4.3281	4.3310	0.0029	0.1028
96	4.1189	4.1235	0.0046	0.1225
120	4.3210	4.3248	0.0038	0.0808
144	4.7066	4.7101	0.0035	0.0620
0.5 M NaCl				
24	10.1661	10.1649	0.0012	0.1276
48	9.9296	9.9324	0.0028	0.1489
72	11.0073	10.9999	0.0074	0.2624
96	10.5844	10.5882	0.0038	0.1011
120	9.5394	9.7620	0.0026	0.0553
144	8.9222	8.9236	0.0014	0.0248
1.0 M NaCl				
24	9.8008	9.8020	0.0012	0.1276
48	10.3737	10.3768	0.0031	0.1648
72	9.6483	9.6548	0.0065	0.2304
96	9.7180	9.7231	0.0051	0.1356
120	9.4903	9.4912	0.0009	0.0191
144	10.6914	10.6920	0.0006	0.0106

sea water). This correlates with the observation in weight difference 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

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, a situation that resulted in the duplex Al-Zn alloy system. Previous studies had suggested that passivation in saline environments was noticed only at media concentrations close to that of sea water (0.3 M NaCl); but this study has revealed that salty environments as low in concentration as 0.1 M also passivates. It is therefore suggested that further investigation should be carried out to establish the minimum molarity of brine at which passivation phenomenon ceases.

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