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Comparative Analysis of the Corrosion Susceptibility of Cast Al-Mn Alloys in Acidic Environments

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Abstract: A study of the effects of the corrosion susceptibility of Al-Mn alloys in varying concentrations of acidic media has been concluded. Al-Mn alloys containing 1.5, 2.5 and 3.5% Mn by weight were cast into rods and machined into cylindrical coupons of average surface area of 13.33 cm^2. The samples were preweighed and immersed in beakers containing 0.25, 0.5 and 1.0 M solutions of H_2SO_4 and HCl solutions, respectively. The set-ups were allowed to stand for 48 h with intermittent withdrawn of a set 12 hourly for corrosion rate characterization. The results showed the usual corrosion trend (prominent in passivating metals) of an initial abrupt increase, followed by a decline, which was maintained in all the media and increased as the percentage of manganese increased. The observed increase in sternness of attack may be ascribed to redistribution in the grain boundary structure of the alloys due to presence of manganese leading to the formation of eutectic phase, which consequently caused mismatch of Al-Mn binary alloy systems.

Key words: Corrosion, aluminium, manganese, passivation, grain boundary, susceptibility, binary alloy systems

INTRODUCTION

Material selection for engineering applications has been hindered by the deterioration of their physio-mechanical properties by large number of diverse environments; even with the broad range of engineering materials modern technology has at its disposal. This makes material selection for a given application of main significance. However, no general rule governs this choice, but a commonsensical decision normally involves a consideration of those properties that are to be conserved in any environment. Despite the cost of high quality, a balance must be struck between cost of frequent replacement/repairs and the ab-initio use of high quality materials (Onuchukwu, 2004). This brings to fore, the dominant role played by corrosion in material selection involving metals which are naturally the most susceptible of all engineering materials to the deleterious effects of corrosion (Ekuma and Idenyi, 2006).

Failures by corrosion occur when the corrosive action renders the corroded device incapable of performing its desired function. Corrosion often interacts synergistically with other failure modes, such as wear or fatigue to produce even more serious combined failure modes, like corrosion wear or corrosion fatigue (Ekuma, 2006). Failure by corrosion and protection against failure by corrosion has been estimated to cost between $8 billion and $128 billion annually in the United States alone (Jones, 1996), exposing the ugly consequences of corrosion globally.

Direct chemical attack is perhaps the most universal type of corrosion. Under this type of corrosive attack, the surface of the machine part exposed to the corrosive media is attacked more

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or less uniformly over its entire surface resulting in progressive deterioration and dimensional reduction of round load-carrying parts over their net cross section (Idenyi *et al*., 2006). However, direct chemical attack may be reduced in severity or prevented by any one or a combination of several means, including selecting proper materials to suit the environment, using plating, flame spraying, cladding, hot dipping, vapour deposition, conversion coatings, and organic coatings or paint to protect the base material, changing the environment by using lower temperature or lower velocity, removing oxygen, changing corrosive concentration or adding corrosion inhibitors, using cathodic protection which supplies electrons to the metal surface to be protected either by galvanic coupling to the sacrificial anode or by an external power supply, or by adopting other suitable design modifications (Shreir, 1994).

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/year and may be calculated as:

$$CPR = \frac{87.6\Delta W}{\rho At}$$

where CPR is the rate of corrosion penetration in mm/year, $\triangle w$ is the weight loss in milligrams; A is the exposed specific area of the specimen in square centimeter, ρ is the density of the specimen in grams per cubic centimeter, t is the exposed time in hours (Callister, 1997). 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 (Ekuma, 2006) and the corrosion form homogeneous otherwise, it becomes somewhat erratic with local instability (Idenyi *et al*., 2006).

The present research is aimed primarily at investigating the service performance of aluminium-manganese alloys in various concentrations of acidic environments H_2SO_4 and HCl media. The outcome of the study is anticipated to be of uttermost significance especially as it regards corrosion design for environments habouring Al-Mn binary alloy systems.

MATERIALS AND METHODS

Materials

This research was carried out in Industrial Physics department laboratory in Abakaliki, Ebonyi state, Nigeria in the month of February 2006. The materials used for the work were scraps of virgin aluminium (99% pure Al) purchased from aluminum stockist in Oshogbo, Osun and manganese procured from Conrod Chemical Company, Enugu. The other materials used were: acetone, stock solutions of tetraoxosulphate (vi) acid and Hydrochloric acid, distilled water, laboratory beakers, measuring cylinders, etc.

Equipments

The equipments used were: drilling machine, lathe machine, and a surface crucible furnace. The basic equipment used was digital weighing machine X21-0014 KERN 770-15, 15402301 that measures to an accuracy of 0.0000001mg which was used to weigh the sample coupons before and after immersion to know the exact weight difference.

Preparation of Test Coupons

The compositions of each of the various Al-Mn alloys were carefully determined. This was separately charged into a surface crucible furnace, then cast into rods after melt down, subsequently machined to sizeable dimensions and afterward, cut into test coupons of dimension range 18×16.95×4.37 mm of initial surface area of about 1333.29 mm^2. Each sample

coupon was drilled with a 5 mm drill bit to provide holes for the suspension of the strings for immersion. Each of the test coupons was carefully polished with emery clothes of 500, 1000 and 1200 m grades to remove carbonized layer, and any initial treatment(s) given to the binary alloys to enable total immersion of the test samples. The samples for Al-1.5% Mn alloy were coded A, Al-2.5% Mn alloy were coded B and that for Al-3.5% Mn alloy were coded C. The samples were preweighed using the highly sensitive digital analytic chemical weighing machine.

Preparation of Environment

The acidic environments adopted for this work were made from hydrochloric acid (HCl) and tetraoxosulphate (vi) acid (H_2SO_4) solutions with three different concentrations each prepared from their stock solutions respectively using normal procedure. The concentrations were 0.25, 0.5 and 1.0 M of the acidic solutions, respectively.

RESULTS AND DISCUSSION

Results

The results of the calculated corrosion rate parameters for the various alloys in different concentrations of tetraoxosulphate (vi) acidic environments are as shown in Table 1-3 while that for the various concentrations of hydrochloric acidic media are as shown in Table 4-6.

Table 1: Corrosion rate data for the various Al-Mn alloys in 0.25 M H_2SO_4 concentrations

Time (h)	Initial Wt. (mg)	Final Wt. (mg)	Wt. Loss (mg)	CPR (mm/year)
Al-1.5% MN				
12	8478.2	8475.1	3.10	0.6288
24	8762.6	8754.3	8.30	0.8417
36	7816.4	7813.7	2.70	0.1825
48	8337.5	8334.0	3.50	0.1775
Al-2.5% Mn				
12	7446.2	7443.3	2.90	0.5882
24	7596.2	7589.3	6.30	0.6389
36	7993.8	7983.4	10.40	0.7031
48	7945.5	7933.7	11.80	0.5983
Al-3.5% Mn				
12	8122.3	8117.3	5.0	1.0141
24	8539.6	8532.3	7.30	0.7403
36	9443.7	9433.0	10.70	0.7234
48	7639.0	7626.6	12.40	0.6288

Table 2: Corrosion rate data for the various Al-Mn alloys in 0.5 M H_2SO_4 concentrations

Time (h)	Initial Wt. (mg)	Final Wt. (mg)	Wt. Loss (mg)	CPR (mm/year)
Al-1.5% Mn				
12	7325.3	7321.2	4.10	0.8316
24	6722.8	6714.4	8.40	0.8518
36	7552.9	7542.2	10.30	0.6964
48	7260.0	7246.7	13.30	0.6744
Al-2.5% Mn				
12	7979.0	7973.9	5.10	1.0344
24	8945.0	8936.0	9.00	0.9127
36	7937.6	7924.2	13.40	0.9050
48	8891.0	8876.4	14.60	0.7403
Al-3.5% Mn				
12	1002.7	9994.4	22.30	4.5231
24	9085.1	9065.8	19.30	1.9573
36	9307.9	9291.2	16.70	1.1291
48	7731.1	7710.3	20.80	1.0547

Table 3: Corrosion rate data for the various Al-Mn alloys in 1.0 M H_2SO_4 concentrations

Time (h)	Initial Wt. (mg)	Final Wt. (mg)	Wt. loss (mg)	CPR (mm/year)
Al-1.5% Mn				
12	7853.3	7848.0	5.30	1.0750
24	7098.5	7088.7	9.80	0.9938
36	6716.7	6704.1	12.60	0.8519
48	7390.9	7374.6	16.30	0.8265
Al-2.5% Mn				
12	8713.7	8707.0	6.70	1.3590
24	8627.0	8616.5	10.50	1.0648
36	1015.5	1013.0	13.50	0.9127
48	8615.8	8601.7	14.10	0.7150
A-L 3.5% Mn				
12	7714.3	7708.4	5.90	1.1967
24	9660.5	9648.8	11.70	1.1865
36	1060.0	1058.7	14.30	0.9668
48	8514.3	8497.3	17.00	0.8620

Table 4: Corrosion rate data for the various Al-Mn alloys in 0.25 M HCl concentrations

Time (h)	Initial Wt. (mg)	Final Wt. (mg)	Wt. loss (mg)	CPR (mm/year)
Al-1.5% Mn				
12	7449.4	7444.7	4.70	0.9533
24	7957.4	7949.7	7.70	0.7809
36	7275.3	7265.1	10.20	0.6896
48	8162.4	8151.4	11.00	0.5578
Al-2.5% Mn				
12	8812.7	8808.1	4.60	0.9330
24	8372.6	8364.4	8.20	0.8360
36	8572.5	8560.8	11.70	0.7910
48	8767.5	8737.5	12.50	0.6338
Al-3.5% Mn				
12	8343.0	8339.9	3.10	0.6288
24	8414.4	8402.4	12.00	1.2169
36	7741.5	7727.6	13.90	0.9398
48	9174.6	9159.5	15.10	0.7657

Table 5: Corrosion rate data for the various Al-Mn alloys in 0.5 M HCl concentrations

Time (h)	Initial Wt. (mg)	Final Wt. (mg)	Wt. loss (mg)	CPR (mm/year)
Al-1.5% Mn				
12	7960.0	7950.5	9.50	1.9269
24	7159.6	7137.0	22.60	2.2920
36	7205.1	7180.2	24.90	1.8939
48	7397.2	7370.9	26.30	1.3336
Al-2.5% Mn				
12	7243.8	7219.5	24.30	4.9287
24	9912.9	9886.8	26.10	2.6469
36	9668.9	9640.7	28.20	1.9066
48	1028.3	1025.7	30.00	1.5009
Al-3.5% Mn				
12	7512.3	7487.1	25.20	5.1112
24	8480.4	8454.4	27.00	2.7382
36	9215.6	9185.6	30.00	2.0283
48	8154.8	8123.4	31.40	1.5922

Discussion of Result

Weight Loss Characterization

A perusal at the Table 1-6 shows a trend of direct relationship between the calculated weight loss values and the various media concentrations and alloy compositions.

Table 6: Corrosion rate data for the various Al-Mn alloys in 1.0 M HCl concentrations

Time (h)	Initial Wt. (mg)	Final Wt. (mg)	Wt. loss (mg)	CPR (mm/year)
Al-1.5% Mn				
12	7187.1	7073.3	113.80	23.0819
24	6883.7	6691.2	192.50	19.5222
36	7970.9	7953.3	251.60	17.0105
48	7614.5	7377.0	237.50	12.0429
Al-2.5% Mn				
12	9569.8	9294.9	274.90	55.7576
24	8687.7	8469.5	218.20	22.1280
36	9083.4	8799.4	284.00	19.2012
48	8176.3	7911.7	264.60	13.4171
Al-3.5% Mn				
12	8656.2	8323.8	332.40	67.4202
24	8252.1	7824.7	460.40	46.6691
36	8612.3	8385.1	227.20	15.3609
48	7912.9	7613.4	299.50	15.1868

Effect of Alloy Composition

From the various tables of the corrosion rate data calculated, it can be inferred that material degradation increased as the fraction of the manganese increased. This may be credited to the increased disparity between aluminium and manganese manifested in the grain boundaries leading to the formation of eutectic phase and hence bimetallic corrosion; as grain boundaries are known to be preferred sites for increased corrosion reaction kinetics. This is evident because, the weight loss increased as a function of the percentage of manganese in the alloy systems in all the environments.

Effect of Media Concentration

A cursory look at the corrosion data tables corroborate that the trend of the corrosion profile varied with time in a manner that depicts a parabolic relation in all the molar concentrations. It can be seen that the trend of the relationship existing between weight loss values and media concentration over the range of exposure time increased as the molar concentration of the acidic environments increased in the aluminium alloy systems. The trend showed initial rapid and steep rise in corrosion rate corresponding to the active region, until a maximum is attained after which, the corrosion rate progressively declined with the exposure time. This is due to the adsorption of the formed oxide film of alumina on the surface of the test samples 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 earlier research (Ekuma, 2006; Ogbonna *et al*., 2004), which suggest that, the initial steep rise in corrosion rate for the composites is thought to be due to increased mismatch between the binary alloy system and the mechanisms: Bimetallic corrosion and possibly crevice attack (Ekuma, 2006) and increase in the diffusion rate of the soluble oxygen enriched media hence increased conductivity in the test environments. The somewhat exponential decrease in corrosion rate is most probably due to immobility of current carrying ions as a result of saturation in the system attributed to the solidity of the naturally formed oxide film; attributed to passivation phenomenon which resulted due to decrease in oxygen solubility hence, reduction in the concentration of the corrosion inducing species. Comparatively, the HCl environments presented the highest corrosion rate values which increased as the molar concentration of the acid increased. This may be attributed to increased ionization rate in the oxygen rich environments which is evidently known to be more in HCl rich environments than in H_2SO_4.

CONCLUSIONS

Passivation was evident in all the media habouring the various weight percentages of manganese in aluminium. However, it was found that the passivation trend diminished as the percentage of the

reinforcing phase (Mn) increased; hence, affirming the general belief that impurity atoms generally reduces the resistance of metals to corrosion attack in aqueous environments.

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