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The Effects of Manganese Addition on the Corrosion Susceptibility of Cast Aluminium Alloy in Acidic Environment

¹C.E. Ekuma, ¹N.E. Idenyi and ²C.D. Ossi

¹Department of Industrial Physics

²Department of Industrial Chemistry, Ebonyi State University,
P.M.B. 053, Abakaliki, Nigeria

Abstract: The corrosion characterization of locally processed Al-Mn alloys containing 1.5, 2.5 and 3.5 Mn by weight has been concluded. The preweighed samples were immersed in beakers containing 0.25, 0.5 and 1.0 M solutions of HCl solutions with the set-ups allowed to stand for 48 h and a set withdrawn 12-hourly for corrosion rate characterization using normal procedure. The results showed normal corrosion rate profile (for passivating metals) of an initial steep rise (active region), followed by a decrease (passive region), which was maintained in all the media and increased as the percentage of reinforcing phase increased. The observed increase in severity of attack may be ascribed to nonhomogeneity in grain boundary distribution; a consequence of bimetallic disparity in the Al-Mn binary alloy systems.

Key words: Corrosion, aluminium, manganese, passivation, binary system

INTRODUCTION

Corrosion is derived from the Latin word *corrodere* meaning gnaw away which occurs as a consequence of a physiochemical interaction between the material, mostly a metal and its environment (Ekuma, 2006). Recognizing that many variables are involved, including environmental, electrochemical and metallurgical aspects may better give us an insight into the intricacy of the corrosion process. For example, anodic reactions and rate of oxidation, cathodic reaction and rate of reduction, corrosion inhibition, polarization or retardation; passivity, effect of oxidizers, effect of velocity, temperature, corrosive concentration, galvanic coupling and metallurgical structure all influence the type and rate of the corrosion process (Idenyi *et al.*, 2006). Also, the statistical nature of corrosion governed by a number of variables can take different forms due to the varied forms of corrosion. For example; microscopic variations in a surface tend to cause different forms of corrosion and also variations in the corrosion rate over a pit area. This has hindered the full elucidation of the mechanism of this undesirable process and subsequently the determination of the necessary preventive techniques (Idenyi *et al.*, 2006).

Metallic corrosion occurs basically as a consequence of their temporal existence in excited state; a refined state due to the absorbed energy during extraction from their ores. This makes them unstable and certain environments provides the possibility for these metals (or alloys) to combine chemically with elements in their environment 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 (Ekuma and Idenyi, 2006).

The rate of corrosion attack can usually be estimated from relatively simple laboratory test in which small specimens of the related materials are exposed to a well-stimulated actual environment with frequent weight change and dimensional measurements carefully taken. The Corrosion Penetration Rate (CPR) usually expressed in mm/year is an important corrosion-monitoring parameter; as it provides corrosion engineers and scientists with reliable information on the service life of materials in environments and may be computed as:

$$R = \frac{87.6W}{\rho At} \quad (1)$$

where R is the rate of corrosion penetration mm/year, W is the weight loss in milligrams; A is the exposed specific area of the specimen in square cm, ρ is the density of the specimen in grams per cubic centimeter and t is the exposed time in hours (Ekuma and Idenyi, 2006). The use of this corrosion rate expression in predicting corrosion penetration in actual service is usually successful if the environment has been properly stimulated in the laboratory (Shreir, 1994) and the corrosion form uniform otherwise it becomes somewhat unpredictable with local disturbances (Idenyi *et al.*, 2006).

The physio-chemical properties of materials are adversely affected by alloying elements, which its somewhat deleterious role in terms of corrosion resistance is diverse and well understood. Though, the alloying element generally improves the mechanical strength of the aluminium alloy, it however diminishes its resistance to corrosion. This is attributed to the highly thermodynamically unstable nature of the compounds formed by these elements that normally settle along the grain boundaries (Ekuma, 2006). This instability predominant in the grain sites is no doubt a good breathing zone for corrosion attack when the material is exposed to corrosive environments. Corrosion experts have attributed cases of intergranular corrosion to this phenomenon (Schweitzer, 1989). The corrosion resistance of aluminium is hampered by the presence of most alloying elements. For instance, elements like zinc, copper, magnesium, manganese, silicon, tin, copper etc, have been attributed to be the cause of most observed corrosion cases in aluminium alloys due to the formation of eutectic compounds. These compounds, which usually exist as phases, create galvanic cells within the matrix, causing flaws on the surface of the alloy, there by creating pits and intergranular cracking (Fontana, 1986).

This present research is aimed at investigating the service performance of Al-Mn alloys in varying acidic concentrations. The outcome of the study is expected to be of great importance in material selection in corrosion design for aqueous acidic environments.

MATERIALS AND METHODS

Materials

This research was carried out in Abakaliki, Nigeria in the month of February 2006. The materials used for this work were scraps of 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, tetraoxosulphate (vi) acid, Hydrochloric acid, distilled water, laboratory beakers, measuring cylinders, etc.

Equipments

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, which measures to an accuracy of 0.0001 g. This 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-Mn 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 coupon samples of dimension range of 18×16.95×4.37 mm and initial surface area of about 1333.29 mm². Each sample coupon was drilled with a 5 mm drill bit to provide holes for the suspension of the strings for immersion. The surface of each of the test sample 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-Mn alloys as to expose its structure for immersion. 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 initial weight of each of the sample coupon was carefully determined using a highly sensitive digital analytic chemical weighing machine.

Simulation of Environment

The environments for this work were acidic environments made from stock solution of hydrochloric acid (HCl) with three different concentrations using normal procedure. The concentrations were 0.25, 0.5 and 1.0 M of the acidic solutions. All corrosion tests were carried out at room temperature.

Constant Immersion Testing

The specimen were polished in a progressively finer grade of emery paper up to 2400 grade with all the test coupons initially cleaned according to ASTM standard G-1-72. The polished and preweighed test coupons were exposed to the stimulated acidic environments for a total period of 48 h.

Experimentation

In each beaker containing the various concentrations of the acids, were suspended 4 samples each of the alloys and the set up allowed to stand for 48 h. A set of coupon was withdrawn 12 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. Then the weight loss also calculated to enable calculation of the corrosion penetration rate in millimeter per year (mm/year) which, was calculated using the weight loss measurements and Eq. 1.

RESULTS AND DISCUSSION

Weight Loss Characterization

A cursory look at the Table 1-3 show a trend of direct relationship between the calculated weight loss values and the various concentration media. The material degradation increased as the percentage of the reinforcing phase increased in all the simulated media. This may be attributed to the increased mismatch 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 favourite sites for increased corrosion reaction kinetics, especially for binary alloys.

Effect of Alloy Composition

From the Table 1-3 of the corrosion rate data calculated, it can be inferred that the percentage of the reinforcing phase diminished the corrosion resistance of aluminium. This is evident because, the weight loss increased as a function of the percentage of manganese in the alloy systems in all the environments. This is in agreement with previous works (Ekuma, 2006; Idenyi *et al.*, 2006) that alloying elements acts as impurities and indeed reduces the degree to which aluminium resists corrosion in stimulated environments.

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

Time (h)	Initial wt. (mg)	Final wt. (mg)	Weight 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	7724.6	13.90	0.9398
48	9174.6	9159.5	15.10	0.7657

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

Time (h)	Initial wt. (mg)	Final wt. (mg)	Weight loss (mg)	CPR (mm/year)
Al-1.5% Mn				
12	7960.0	7905.5	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

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

Time (h)	Initial wt. (mg)	Final wt. (mg)	Weight 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 Media Concentration

A cursory look at the corrosion data Table 1-3 confirm that the trend of the corrosion rate varied albeit parabolically with time in all the molar concentrations and it can be seen that the trend of direct relationship existing between weight loss values and media concentration over the range of increasing exposure time with the loss increasing 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 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 suggest that, the initial steep rise in corrosion rate for the composites is thought to be due to increased mismatch between the matrix and the mechanisms: bimetallic corrosion and possibly crevice attack and pitting corrosion (Ekuma, 2006); and increased diffusivity 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 phenomenon attributed to the stability of the naturally formed oxide film; a consequence of passivation phenomenon which set in due to reduced oxygen solubility hence, decrease in the concentration of the corrosion inducing species. Comparatively, the 1.0 M HCl presents the highest corrosion rate.

Corrosion Rate Profile

The observed corrosion rate profile is in agreement with that of passivating metals subjected to acidic environments, which aluminium is known to belong. The observed initial rapid and steep rise in corrosion rate which peaked at the 12 h exposure time corresponds to the active region while the region that progressively declined with the time of exposure corresponds to the passive region. 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 (Idenyi *et al.*, 2006).

CONCLUSION

The various alloy compositions was found to passivate in all the media over the time of exposure. However, the general corrosion behaviour shows that the corrosion resistance of the alloys was found to diminish as the percentage of the reinforcing phase increased. It was also observed that the corrosion susceptibility increased with increasing media concentration. This behaviour agrees with theoretical affirmation that alloying elements tend to reduce the corrosion resistance of metals subjected to acidic environments. This is attributed to increased grain boundary concentrations which are known to be approving sites for corrosion kinetics.

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