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Full Length Research Paper

Reduction of corrosion in various concentrations of hydrochloric acid by compositional design

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Experimental analysis has been advanced in the reduction of corrosion in various concentrations of hydrochloric acid (HCI) by compositional design. The analysis which involved metal matrix composite design and corrosion pattern determination by weight loss method and least square model showed that percentage weight loss, corrosion rates and reactivity decreased as Aluminum addition in the Al/Fe composite increases. The evolved composite reaction in the media solution followed a first order equation pattern in which concentration decreases with time. With respect to the uncombined Iron (Fe) metal material, analyses showed that 30wt%Al/70wt%Fe composition reduced corrosion by 50% and is fairly sustainable and stable under severe harsh environment.

Key words: Weight loss, hydrochloric acid (HCI), corrosion.

INTRODUCTION

Materials in one form or the other undergo transformation (aging) in either shape or content. One of the most important forms of aging involves corrosion. Corrosion damage is possible because of aggressive or harsh environmental conditions which these materials are vulnerable to, and environmental corrosivity varies from metal to metal. When a material is degraded by corrosion, another subsequent process causes failure, for instance, metal thinning and mechanical overload or pitting that compromises hermeticity (Braithwaite et al., 2011; Aarao et al., 2006). At room temperature, most chemical compounds of metals have lower value (more negative) of Gibbs free- energy ΔG than the uncombined metals; therefore most metals have an inherent tendency to Corrode. The tendency for any chemical reaction to occur, including the reaction of a metal with its environment is measured by the Gibbs free-energy change, ΔG . The more negative the value of ΔG , the greater the tendency for the reaction to occur, (Revie and Uhlig, 2008). However, the tendency for metal to corrode does not depend on reaction rate but may electrochemically depend on the value of corrosion cells

In consideration of these phenomena, engineers, material scientists and scientists are making serious efforts to improve the quality of materials through the process of composite development. Composite materials are improved materials having two or more distinct parts or phase. They are design with the aim of having better properties over monolithic materials (Ihom et al., 2012). Corrosion resistance of a material is an essential property of the material. The corrosion of a composite material is affected by two factors; the specificity of a given corrosion towards the individual components and galvanic interactions between them. Appreciating this, Fontana (1987) emphasized the importance of evaluating composites in a number of environments which they may likely be applied in. This position has been considered by previous researchers, amongst who are; Ihom et al. (2012), the work evaluated the corrosion resistance of aluminum alloy matrix/2.5% particulate glass reinforced composite in: HCI, NaOH, and NaCI solutions. Their findings led to their conclusion, that the composite cannot be use in NaOH and HCI environments but NaCI. electromotive force (emf).

Darvishi et al. (2010) investigated the impact of iron and manganese concentration on the morphology of complex intermetallics and their influence on the mechanical properties and microstructures of AI-16.67wt. % Si alloy using 0.4, 1.2 and 1.8 irons content and Mn content of 0.6 and 0.9 wt. %. Findings revealed that as iron increase, the UTs steadily decreased from 229 mpa at 0.4 wt.% of Fe to 187 mpa of Fe content at 1.8 wt.%. Other works include: Owate and Chukwuocha (2008), Owate et al. (2012), Khraisat and Jadayil (2010), Mamatha et al. (2011), Asuke et al. (2009) and Tjong and Ma (1997). The purpose of this work is to investigate the corrosion behavior of iron/aluminum composite in HCI environment. The least square model is employed in the analysis of the experimental data through a computer programme - maple.

MATERIALS AND METHODS

Materials and apparatus used for this work include, aluminum and iron materials composite prepared using the cast method, solution of 20% NaOH, ethanol, water, abrasive paper, vernier caliper, brush, digital weighing balance, flat bottomed flasks, and suspension thread, Dil. H_20 and GallenKamp Muffle.

Scraps of Aluminum and iron materials which were bought were weighted in kilogram, using a spring weighing balance. The materials were electrically cleaned by scrapping using an electronic abrasive papers No. 120 device, Einhell 201 to a shining surface, dipped into a solution of 20% NaOH, washed with plenty of water and degreased in absolute ethanol, and finally compose in the ratio of; 1:9, 2:8 and 3:7 percentage by weight. The compositions were 10wt%Al/90wt%Fe, 20wt%Al/80wt%Fe and 30wt%Al/70wt%Fe, respectively.

The compositions were cast into a molten furnace, the formed composite was machined into coupons of various sizes and weights measured in gram (g) using an electronic weighing balance, scientech, model SA 210. The coupons were tagged according to the percentage composition and molar concentration of the expected media solution. A hole of 2.0 mm diameter was drilled at the topside of each of the coupon to allow for passage of suspending thread. Coupon were sand paper to through shining surface, dipped into a solution containing 200 g of NaOH dissolved in 800 ml of deionized water (H₂0) washed in plenty of water and degreased in absolute ethanol (99.9% ethanol). They were later washed with acetone and dried in a Gallenkamp muffle furnace at a temperature of 30°C. The various concentrations of HCl of 0.5 M, 1.0, 1.5, 2.0 and 3.0 M, were prepared.

The various molar concentrations were put into five respective beakers of 250 ml, adding up to fifteen beakers. The coupons were immersed into the beaker with the help of the suspending thread. Retrieved progressively every 24 h for 240 h (ten days). The corrosion process was monitored by reweighing the coupon. The difference in weight was recorded, and weight loss and corrosion rate determined.

RESULTS

Pattern analysis

The least square model; to have an overview of the behaviour of the composite in corrosive media and to be

able to predict what the situation would be in time (t) assuming the molar concentration and weight of composite material remained the same, a regression analysis is carried out on the data.

$$Log (w_i - \Delta w) = a (t) + b$$
 (1)

Where a and b are constant, called the regression coefficients. The entire process was readily done through a software package –Maple.

The observed pattern

The decay shows that reactivity was on decrease as time and Aluminum percentage in the matrix increases Atkins and Pauls (2006). The evolved composite reaction followed a first order equation pattern in which concentration decreases with time.

$$\ln \left[{}^{[A]/[A]}_{o} \right]_{=} -kt$$
 (2)

$$[A] = [A]_{o}e^{-kt}$$
(3)

DISCUSSION

The impact of corrosion is most felt on structures as it attacks their functional stability and reduces safety. To address this, various methods are adopted, but each remains a function of time as none is actually foolproof. Metal matrix composite method was applied here. Results presented in Tables 1 and 2 indicate that weight loss was linearly increasing with increase in media concentration. This finding agrees with those of Aarao et al. (2006), Zhang et al. (2001), Owate et al. (2008) and Denpo et al. (1997). The weight loss in both the composite and uncombined material can be explained in terms of chemical reaction, the electrochemical nature of corrosion can be adopted:

$$AI \rightarrow AI^{3+} + 3e \tag{4}$$

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \tag{5}$$

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \tag{6}$$

Two possible overall reactions are;

$$2AI + 6HCI \rightarrow 2AICI_3 + 3H_2$$
 (hydrogen evolution) (7)

$$2H^+ + 2e \rightarrow H_2 \tag{8}$$

 $4AI+3O_2 \rightarrow AI_2O_3$ (tenacious oxide film formation) (9)

Equations 4 and 6 are partial reactions, both must occur simultaneously and at the same rate on the metal surface. Ihom et al. (2012) stated that "during metallic

S/N	Log (w _i - Δw) Experimental	Log (w _i – Δw) Analytical	% Error	% Weight Loss Δw/wi ¹⁰⁰ / ₁
1	1.5824	1.5802	0.1373	5.000
2	1.5745	1.5802	0.3588	6.7000
3	1.5675	1.5801	0.7979	8.2000
4	1.5639	1.5801	1.0224	8.9450
5	1.5598	1.5800	1.2772	9.8000
6	1.5521	1.5799	1.7612	11.4000
7	1.5417	1.5799	2.4176	13.000
8	1.5341	1.5799	2.8971	15.0000
9	1.5253	1.5798	3.4511	15.7000
10	1.5169	1.5798	3.9794	18.3000

Table 1. Corrosion behaviour of uncombined Fe material in 0.5 MHCl.

Table 2. Corrosion behaviour of (30wt.%Al/70wt.%Fe) composite in 0.5 MHCI

S/N	log (w _i - Δw) Experimental	Log (w _i – ∆w) Analytical	% Error	% Weight Loss Δw/wi ¹⁰⁰ / ₁
1	1.6932	1.6872	0.3546	2.1500
2	1.6818	1.6872	0.3205	4.0000
3	1.6818	1.6872	0.3198	4.6700
4	1.6790	1.6872	0.4851	5.3000
5	1.6776	1.6872	0.5674	5.6000
6	1.6754	1.6872	0.6797	6.0000
7	1.6718	1.6872	0.9106	6.8400
8	1.6684	1.6872	1.1116	7.5700
9	1.6645	1.6872	1.3428	8.4000
10	1.6610	1.6871	1.5482	9.1400

corrosion, the rate of oxidation equals the rate of reduction, in terms of electron production and consumption". This is affirmed by Fontana (1987) who noted that the partial reactions can be used to interpret virtually all corrosion problems. Equation 9 is the overall equation which gave rise to deposition of aluminum oxide film on the surface of the composite as shown by the determined corrosion rate of 0.15 mdd and percentage weight loss of 9.3%. Under normal circumstance the corrosion rate must have been slowed down more than what has been noted, owing to the fact that in the presence of oxygen, aluminum forms a tenacious oxide film (Khanna, 2008). This was not absolute, because at the cathode two cathodic reactions were possible; the evolution of hydrogen, Equation (8) and the reduction of oxygen. On the surface of the composite there are two electrons consuming reactions. Since the rates of oxidation and reduction must be equal, increasing the total reduction rate invariably increases the of aluminum dissolution.

The above situations explain why weight loss can still be notice despite Aluminum addition. Aluminum is also likely going to dissolve in aqueous sodium hydroxide solution use in terminating corrosion process.

 $2AI + 2Na0H + 6H_20 \rightarrow 2NaAI (0H) 4 + 3H_2,$

According to Fontana (1987) Aluminum is a reactive metal, but it develops an aluminum oxide coating or film that protects it from corrosion in many environments. This film is quite stable in neutral and many acid solutions, but is attacked by alkalis. This statement is supported by the results of Ihom et al. (2012) that showed that aluminum composite has a poor resistance in NaOH solution.

Fe oxidizes thus:

 $2Fe(s) \rightarrow 2Fe_2$ + (aq) + 4e-

 O_2 in media are reduced thus;

 O_2 (g) + 4H+ (aq) + 4e- \rightarrow 2H₂O (l)

Since it is amphoteric.

Fe also is slightly amphoteric and is attacked by concentrated Na0H, (Lee, 2008), however this is not too pronounced as Al undergoes passivation, and therefore

Time (day)	20wt%Al/80wt%Fe Rate constant, K(day-1)	10wt%Al/90wt%Fe Rate constant, K(day-1)	Uncombined Fe Material Rate constant, K(day-1)
1	9.0 x 10 ⁻⁴	1.0 x 10 ⁻⁴	2.1 x 10 ⁻³
2	8.0 x 10 ⁻⁴	9.0 x 10 ⁻⁴	1.4 x 10 ⁻³
3	7.0 x 10 ⁻⁴	8.0 x 10 ⁻⁴	1.2 x 10 ⁻³
4	5.0 x 10 ⁻⁴	6.0 x 10 ⁻⁴	1.0 x 10 ⁻³
5	5.0 x 10 ⁻⁴	5.0 x 10 ⁻⁴	8.0 x 10 ⁻⁴
6	5.0 x 10 ⁻⁴	6.0 x 10 ⁻⁴	8.0 x 10 ⁻⁴
7	4.0×10^{-4}	5.0 x 10 ⁻⁴	8. 0x 10 ⁻⁴
8	5.0 x 10 ⁻⁴	6.0 x 10 ⁻⁴	8.0 x 10 ⁻⁴
9	4.0×10^{-4}	7.0 x 10 ⁻⁴	8.0 x 10 ⁻⁴
10	4.0 x 10 ⁻⁴	7.0 x 10 ⁻⁴	8.0 x 10 ⁻⁴



Figure 1. Rate constants of Corrosion of uncombined Fe metal, composites of (10wt. % Al/90wt. % Fe) and (20wt. % Al/80wt. %Fe) in 0.5 MHCI.

can be transitional. This line of thought is formed by result of Tables 1 and 2. Examination of Table 3 and Figure 1 shows the rate constant, which indicates that;

the reactivity was decreasing with time as Aluminum addition increases. For the uncombined, the reactivity reduced from 2.1 × 10^{-3} to 8.0 × 10^{-4} , while in the



Figure 2 Showing graph the weight loss against time for 30wt%Al/70wt% Fe composite.



Figure 3. Showing the micrograph of 30wt%Al/70wt%Fe.

20wt.%Al/80wt.%Fe it reduced from 9.0×10^{-4} to 4.0×10^{-4} Comparatively the reactivity stood at 8.0×10^{-4} in the tenth day in the uncombined metal material but was 4.0×10^{-4} in 20wt.%Al/80wt.%Fe (Figure 2). In our

first considered case of time, reactivity was decreasing with time, showing that concentration was probably decreasing, confirming that the chemical reaction followed first order equation pattern in which concentration decreased with time (Altkin, 2008 and Melchers, 2006).

$$[A] = [A] 0e^{-kt}$$
 (4)

The second case, expressed the activity of Aluminum in terms of passivation, by its oxide formation. Passivition is most likely enhanced if the hydration energy of the formed oxide does not exceed the lattice energy. Aluminum oxide (Al_2O_3) with atomic weight of 101.96 g is likely not large enough to have decreased lattice energy which favours increased solubility.

The micrograph in Figures 3 and 4 revealed the dominance of Fe containing intermetallics leading to increase in UTs with decrease in hardness, as aluminum percentage increases, the trend agrees with the finding of Darvishi et al. (2010). Post corrosion coupon physical examination confirmed result. From the discussion, it is obvious that corrosion was reduced by compositional design. Analysis showed that 30wt.% Al/70wt.%Fe composite will be fairly stable and sustainable under harsh environment.



Figure 4. Showing the micrograph of 20wt%Al/80wt%Fe.

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