

THE CORROSION BEHAVIOUR OF Al – Mn BINARY ALLOY SYSTEMS IN SELECTED ENVIRONMENTS

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ABSTRACT

A study of the corrosion trends of Al - Mn duplex alloys in selected environments has been carried out. Al - Mn alloys containing 1%, 2%, 3% and 4% Mn by weight were cast into rods and machined into cylindrical test samples of average surface area of 24.10cm². The preweighed samples were subjected to 0.1M solution of HCl, seawater and atmosphere respectively. The set-ups were allowed to stand for 672 hours with a set withdrawn 168-hourly for corrosion rate characterization. The results obtained were in conformity with those of passivating metals (or alloys) in simulated environments. There was an initial steep rise in corrosion rate accompanied by a gradual decline as the exposure time increased. Comparatively, the atmospheric environment presented the least corrosion attacks, followed by seawater, while the 0.1M HCl environment showed the worst corrosion attacks on the samples.

Keywords: Corrosion, Passivation, Binary alloy, Aluminium, Manganese

I INTRODUCTION

The basic properties of metals (or alloys) are of paramount importance during fabrication, application and other various vicissitudes of engineering material applications. The physical and mechanical properties such as ductility, malleability, resistance to fatigue (or resistance in diverse environments), weldability, hardness, toughness etc grossly affect the service performance of these materials. The need to develop engineering materials of high strength to weight ratio with relatively good corrosion resistance in diverse environments is a crucial one [1]. This has led to the increased research by corrosion experts in the possible adaptation of aluminium base alloys as structural materials.

The effects of atmosphere on the corrosion behaviour of metals are probably the most common form of corrosion. Therefore, it is important to know the specific corrosion rate in a given application environment in order to effectively use metals in outdoor structures [2]. Most of the broad forms of corrosion occur in the atmosphere and some appear to be largely restricted to it [3]. Since the corroding metal is not bathed in large quantities of electrolyte, most atmospheric corrosion operates in highly localized corrosion cells. Most aluminum alloys have excellent resistance to atmospheric corrosion (often called weathering), and in many outdoor applications, such alloys do not require shelter, protective coatings or maintenance [4].

Basically, seawater is a complex composition of different dissolved minerals [5], but, a single parameter of interest in defining the complexity of seawater is the chlorinity and is of practical importance because, it is present in large amount both in seawater, road salts, and some soils and in lower concentration in other natural sources [3].

A general method for estimating the useful life of metals (or alloys) has been the use of various types of metals and alloys for the different types of atmospheres. Recognition of marked differences in corrosivity has made it convenient to divide atmospheres into types: rural, urban, industrial, marine, or a combination of these [2].

The stability of metals (or alloys) in an aggressive environment largely depend on the protective properties of organic or inorganic films as well as on the layer of corrosion products. Some film properties, such as chemical composition, conductivity, adhesion, solubility, hygroscopicity, and morphology, determine its ability as controlling barrier to different kinds of attack and corrosion rates [6]. On the other hand, the stated characteristics depend, in turn, on chemical composition and metallurgical history of the metal (or alloy), physicochemical properties of coating, and on environmental variables such as atmospheric conditions, type and amount of pollutants, wet-dry cycles, etc. [2; 7].

Aluminium owes its excellent corrosion resistance and its usage as one of the primary metals of commerce to the barrier oxide thin film – alumina which has a strong affinity for oxygen. However, in environments harbouring aluminium (and some of its alloys), this oxide thin film assists in the formation of passive micro – 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 abraded, re-forms instantaneously in most environments [8].

The rate of material removal as a consequence of its physiochemical (or physiomechanical) interaction is better evaluated in terms of the corrosion penetration rate (CPR) expressed mainly in mm/yr or mils/yr. it is an important corrosion evaluation parameter as it gives enough information to corrosion experts on the performance of any engineering material in service especially when there is minimal local instability. This corrosion penetration rate is normally computed based on the formula:

$$CPR = \frac{k \Delta w}{\rho A t} \quad (1)$$

where Δw is weight difference after exposure time t , ρ and A are density and specific exposure area of specimen respectively, and k is a constant whose magnitude depends on the system of units used. For this work, $k = 87.6$ and CPR is in mm/yr, where Δw , t , ρ and A are expressed in mg, hrs, g/cm^3 and cm^2 respectively [1].

The objective of the present research is to characterize and investigate the corrosion susceptibility of Al – Mn alloys (Al – 1.0%Mn; Al – 2.0%Mn; Al – 3.0%Mn and Al – 4.0%Mn) in diverse environments (seawater, 0.1M HCl environment and atmosphere). The importance of these environments is overwhelmingly known. The seawater environment is known to contain the aggressive chloride ion, hence

represents a positively saline environment; the 0.1M HCl acidic environment is relatively the mean concentration of most environments harbouring aluminium alloys while the natural atmosphere represents the outdoor application of aluminium alloys. Hence, it is envisaged that the present research will be of importance in choosing the various Al – Mn alloys both in general corrosion design and in structural applications.

II EXPERIMENTAL TECHNIQUES

Study Area

This experiment was carried out in Abakaliki, South – Eastern Nigeria between the months of November and December 2007.

Materials/Equipment

The materials used for this work were sourced locally from Enugu – Nigeria. They include virgin aluminium (99% pure Al) purchased from aluminum stockist and pure granulated manganese 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, a surface crucible furnace and analytic digital weighing machine with an accuracy of 0.0001g.

Specimen Preparation

After the aluminium scraps had been rid of clogs of macro dirt to avoid contamination of its percentage purity and possible degradation of its casting properties, computation for each of the Al – Mn alloy compositions were carefully worked out and charged into the surface crucible furnace. The molten alloys were cast into rods after melt down, machined to significant dimensions and then, cut into test samples of initial surface area of about 24.1041cm². Each sample coupon was drilled with a 5mm drill bit to provide hole for the suspension of the strings. The surface of each of the test coupon was then thoroughly polished with emery clothes according to ASTM standard. The samples for 1% Mn-99% Al alloy were coded **A**; 2% Mn-98% Al alloy were coded **B**; 3% Mn-97% Al alloy were coded **C** and 4% Mn-96% Al alloy were coded **D**.

Simulation of Environment

The environments for this work were seawater which was source from Ndibe beach in Afikpo, Ebonyi – Nigeria; 0.1M HCl prepared using normal procedure and the natural atmosphere.

Design Setup and Experimentation

The test coupons were divided into three groups of 4 test coupons each. The first group was exposed to atmospheric environment while the others were immersed in seawater environment and 0.1M HCl environment respectively. The method adopted for this research is the weight loss technique. The set up was allowed to stand for 672 hours with a set of coupon withdrawn 168 hourly, (washed with distilled water, cleaned with acetone and dried in open air before weighing to determine the final weight using the digital analytic weighing machine) for corrosion characterization.

III RESULTS AND DISCUSSION

Results

Tables 1 – 4 show the table of the corrosion trend parameters for the alloys in the various environments being studied.

Discussion of Result

Seawater Environment:

A perusal at Tables 1 – 4 shows that there was significant passivation of the various alloy samples in the seawater environment. This is in tandem with earlier observation that aluminium – based alloys passivate in environments that are positively saline [9; 10] and also in agreement with literature [11]. The corrosion penetration rate values show that all the alloy samples were relatively passive in the environment.

Atmospheric Environment:

Taking a look at the corrosion rate parameters (Tables 1 – 4), it can be inferred that the various alloys being characterized relatively exhibited the phenomenon of passivation. The observed low level of attack by atmospheric constituents may be attributed to the rapid formation of the passive oxide film – alumina on the alloy surfaces which uttermostly prevents further attack. This is again in agreement with literature as aluminium-based alloys are known to have good corrosion resistance in outdoor applications [12].

Acidic Environment:

From tables 1-4, it can be inferred that weight loss increased with time in the aluminium alloy system. The trend conformed to initial observations [13; 14] that the degradation of materials in acidic environments has a direct consequence on the media concentration. It can also be inferred that material degradation increased as the fraction of the manganese increased. This may be attributed to the increased disparity between aluminium and manganese manifested in the grain boundaries leading to the formation of eutectic phase as grain boundaries are known to be favourable sites for increased corrosion reaction kinetics. Generally, the corrosion rate increases with increase in the molar concentration of the test environment. However, the overall trend of the corrosion profile clearly depicts that of passivating metals subjected to simulated environments. It showed initial rapid increase in corrosion rate (active region), until a limit is attained (passivation phenomenon sets in) after which, the corrosion rate gradually declined with the exposure time (passive region). This may be attributed 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 [2]. The somewhat exponential decrease in corrosion rate is most probably due to immobility of current carrying ions as a result of diffusion phenomenon; leading to the stability of the naturally formed oxide film. This trend is in conformity with existing theories suggesting that media saturation could be an important corrosion – monitoring index during passivation. This is so because the rate of deposition would be slowed down by ion mobility, which is generally low for extremely saturated media due to drastic reduction in oxygen mobility.

IV CONCLUSION

The study of the corrosion trend of various Al – Mn alloys has been concluded. Passivation phenomenon was evident in all the environments harbouring 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. Comparatively, the atmospheric environment showed the least corrosion attacks on the samples; seawater in-between; and 0.1M HCl environments the worst attacks.

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Table 1: Corrosion Rate Data for Al – 1.0% Mn in the various Environments

Time (Hours)	Initial Wt. (g)	Final Weight (g)	Weight Diff. (g)	Corrosion Rate (mm/yr)
SEAWATER ENVIRONMENT				
168	12.4780	12.5158	0.0378	0.3024
336	12.6150	12.6138	0.0012	0.0048
504	11.7506	11.7543	0.0037	0.0099
672	13.4928	13.4914	0.0014	0.0028
0.1M HCl ENVIRONMENT				
168	14.1051	13.9950	0.1101	0.8808
336	13.1971	13.0940	0.1031	0.4124
504	13.0728	12.8680	0.2048	0.5461
672	11.7302	11.5908	0.1394	0.2788
ATMOSPHERIC ENVIRONMENT				
168	11.7314	11.7317	0.0003	0.0024
336	13.1392	13.1376	0.0016	0.0064
504	12.1188	12.1230	0.0042	0.0112
672	13.4997	13.4972	0.0025	0.0050

Table 3: Corrosion Rate Data for Al – 3.0% Mn in the various Environments

Time (Hours)	Initial Wt. (g)	Final Weight (g)	Weight Diff. (g)	Corrosion Rate (mm/yr)
SEAWATER ENVIRONMENT				
168	13.2045	13.2039	0.0006	0.0048
336	12.5933	12.5947	0.0014	0.0056
504	12.0890	12.1201	0.0311	0.0829
672	12.9553	12.9534	0.0019	0.0038
0.1M HCl ENVIRONMENT				
168	12.5930	12.4200	0.1730	1.3840
336	12.6872	12.4726	0.2146	0.8584
504	12.9527	12.7041	0.2486	0.6629
672	13.2930	13.0422	0.2508	0.5016
ATMOSPHERIC ENVIRONMENT				
168	12.4668	12.4670	0.0002	0.0016
336	12.2723	12.2732	0.0009	0.0036
504	13.1319	13.1318	0.0001	0.0003
672	13.2279	13.2265	0.0014	0.0028

Table 2: Corrosion Rate Data for Al – 2.0% Mn in the various Environments

Time (Hours)	Initial Wt. (g)	Final Weight (g)	Weight Diff. (g)	Corrosion Rate (mm/yr)
SEAWATER ENVIRONMENT				
168	13.3548	13.3493	0.0055	0.0440
336	12.9233	12.9139	0.0094	0.0376
504	12.5408	12.5451	0.0043	0.0115
672	10.8676	10.8810	0.0134	0.0268
0.1M HCl ENVIRONMENT				
168	14.1137	13.9905	0.1232	0.9856
336	11.8872	11.6810	0.2062	0.8248
504	12.4073	12.2774	0.1299	0.3464
672	12.8719	12.4848	0.3871	0.7742
ATMOSPHERIC ENVIRONMENT				
168	12.7563	12.7566	0.0003	0.0024
336	13.7782	13.7790	0.0008	0.0032
504	12.1569	12.1537	0.0032	0.0085
672	12.3274	12.3291	0.0017	0.0034

Table 4: Corrosion Rate Data for Al – 4.0% Mn in the various Environments

Time (Hours)	Initial Wt. (g)	Final Weight (g)	Weight Diff. (g)	Corrosion Rate (mm/yr)
SEAWATER ENVIRONMENT				
168	11.5970	11.5952	0.0018	0.0144
336	12.0754	12.0728	0.0026	0.0104
504	12.4775	12.4716	0.0059	0.0157
672	13.7434	13.7403	0.0031	0.0062
0.1M HCl ENVIRONMENT				
168	12.7531	12.5696	0.1835	1.4680
336	12.3776	12.0560	0.3216	1.2864
504	12.8965	12.5716	0.3249	0.8664
672	12.6254	12.2466	0.3788	0.7576
ATMOSPHERIC ENVIRONMENT				
168	13.0764	13.0766	0.0002	0.0016
336	12.5558	12.5559	0.0001	0.0004
504	13.3783	13.3777	0.0006	0.0016
672	11.8402	11.9098	0.0696	0.1392