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The Influence of Media Concentrations on the Passivation Layer Characteristics of Al-Zn Alloys in Brine Environment

[1]C.E. Ekuma, [1]N.E. Idenyi, [2]F.K. Onwu and [1]A.E. Umahi
[1]Department of Industrial Physics,
[2]Department of Industrial Chemistry, Ebonyi State University,
P.M.B. 053, Abakaliki, Ebonyi, Nigeria

Abstract: Corrosion tests were carried out on locally processed aluminum-based alloys with varying weight percentages of zinc. Test coupons of dimensions 17×16.8×15 mm were machined from the as-cast alloy to an average surface area of 1271 mm^2. The coupons were immersed in 0.1, 0.25, 0.5 and 1.0 M NaCl solutions with a coupon withdrawn simultaneously from each medium at 24 hourly rate for characterization. The results revealed that the coupons gained weight in all the media indicating the phenomenon of passivation; with the greatest layer thickness observed in the range 0.25 to 0.5 M brine. This behavior is attributed to the increasing electrical conductivity of the solutions; a consequence of increasing solubility of the media which progressively increased peaking within this range and hence, increased passivation kinetics before declining due to the immobility of current carrying ions.

Key words: Layer thickness, passivation kinetics, aluminium alloy

INTRODUCTION

Corrosion derived from the Latin word corrodere meaning gnawed away, occurs as a consequence of a physico-chemical interaction between material, mostly a metal and its enviroument, of which the driving force is the free energy of the system which is generally lowered by the reaction of the metal to form a metal oxide of stable state (Ekuma and Idenyi, 2006). The corrosion process takes place at the material-medium interface and therefore, is a heterogeneous reaction in which the structure and condition of the metal surface have a significant role in determining the corrosion behaviour of metals and its alloys in any enviroument (Idenyi and Ekuma, 2006).

The complex nature of the corrosion process may be better appreciated by recognizing that many variables are involved, including enviroumental, electrochemical and metallurgical aspects. 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, media concentration, galvanic coupling and metallurgical structure, all influence the type and rate of the corrosion process (Idenyi Ekuma and Owate, 2006).

The various types of corrosion are distinguished and include among others, direct chemical attack, galvanic corrosion, crevice corrosion, pitting corrosion, intergranular corrosion, stress corrosion cracking etc; all based on visual appearance (Callister, 1997), but recent studies have expanded the corrosion categories redefining them by mechanism rather than by visual appearance (Idenyi *et al*., 2006). Depending on the type of enviroumeuts, loading and mechanical function of the machine parts involved, any of the types of corrosion may combine their influence with other failure modes to produce premature failures. Of particular concern are interactions that lead to failure by corrosion wear, corrosion fatigne, fretting fatigne and corrosion induced fracture (Kruger, 2001).

Corresponding Author: C.E. Ekuma, Department of Industrial Physics, Ebonyi State University, P.M.B. 053, Abakaliki, Ebonyi, Nigeria Tel: 2348034382467, 2348033385069, 234805845457

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 dimensioual measurements carefully taken. The corrosion penetration rate (CPR) or the rate of material removal as a consequence of the physico-chemical interactions mostly expressed in mils $year^{-1}$ or mm $year^{-1}$ is an important corrosion-monitoring index that gives reliable information to corrosion experts on the rate of corrosion progress on a given material in service. The mathematical computation of CPR is based on the formula

$$\mathrm{CPR} = \frac{k\Delta W}{\rho A t} \tag{1}$$

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 $year^{-1}$, where, w, t, ρ and A are expressed in mg, hrs, g cm^{-3} and cm^2, respectively (Callister, 1997). For most applications, a corrosion penetration rate of less than about 0.50 mm $year^{-1}$ is tolerable. However, this inference is suitable only for uniform corrosion and becomes somewhat unreliable with local instability (Ekuma *et al*., 2006).

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 properly characterized (Ekuma *et al*., 2006). For instance, the passivity of some normally active metals and alloys in a given environmental condition where they lose their chemical reactivity and become immune to corrosion attack may be reverted to active state by altering the character of the environment, for instance, fluid velocity. 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 metal-environment interface at relatively 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 and if abraded, repassivates immediately (Frankenthal and Kruger, 1978); hence, the conditions that promote corrosion of alnminnm and its alloys, therefore, must be those that continuously abrade the film mechanically or promote reactions that locally degrade this protective oxide film by minimizing the availability of oxygen to rebuild it (Idenyi *et al*., 2006). It should be noted that all breakdown mechanisms involve damaging species. Unfortunately, one of the major damaging species causing breakdown of passivity is the aggressive chloride ion, which is abundantly available in nature (Eknma *et al*., 2006). Even at that, alumininm has excellent corrosion resistance, a consequence of barrier oxide film-the alumina (Al_2O_3) and this is the reason for its usage as one of the primary metals of commerce. Alumininm has a strong affinity for oxygen and in environments habouring alnmininm (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 (Eknma *et al*., 2006).

The need for the present study is obvious. Al-Zn alloys have diverse uses in industries and in different environments. Again, the aggressive chloride ion (in brine) is of uttermost practical importance because of its large amount both in sea water, road salts and some soils. Hence, the need to understand the corrosion behaviour of these alloys in environments that are positively alkaline.

MATERIALS AND METHODS

Materials/Equipment

The investigation of the influence of media concentrations on the passivation layer characteristics of Al-Zn alloy systems in sodium chloride solution was carried out in Abakaliki, Ebonyi State, South-Eastern Nigeria between the month of October and November 2005.

The materials used for this work were virgin 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 X21-0014 KERN 770-15, 15402301 which measures to an accuracy of 0.0000001 mg that is used to weigh the test coupons before and after immersion to know the exact weight difference.

Specimen Preparation

After the computation for each of the Al-Zn alloy compositions have been 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 dimension range of 17×16.8×15 mm with initial surface area of about 12.71 cm^2. Each sample coupon was drilled with a 5 mm drill bit to provide hole for the suspension of the strings. The surface of each of the test coupon was thoroughly polished with emery clothes according to ASTM standard G-I-72 as to remove any oxide layers, carbonized layer and any initial treatment(s) given to the Al-Zn alloy as to expose of 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 the highly sensitive digital analytic chemical weighing machine, which measures to an accuracy of 0.0000001 mg.

Simulation of Environment

The enviroumments for this work were alkaline enviroumments with four different concentrations made from sodium chloride salt using normal procedure. The concentrations were 0.1, 0.25, 0.5 and 1.0 M of the alkaline solutions.

Experimental Setup

In each beaker containing the various concentrations of NaCl were suspended six samples each of the alloys and the set up allowed to stand for 144 h. A set of coupon was withdrawn 24 hourly, washed with distilled water, cleaned with acetone and dried in an open air. The final weight of each of the test sample was determined using the digital analytic weighing balance.

Theory of Scale Film Deposition

The scale film (SF) deposited on the surfaces of the sample coupons were evident as there was significant weight increase in all the test coupons in the varying brine concentrations. The scale film thickness was however carefully calculated using the empirical formula:

$$SF = \frac{\Delta W}{A} \tag{2}$$

where, Δw is the weight difference in milligram; A is the specific surface area in mm^2.

Theory of Deposition Rate

The Deposition Rate (DR) no doubt gives the insight of the material adsorption trend in any passivating environment. To evaluate this, an empirical mathematical model:

$$\mathrm{DR} = \frac{\Delta W}{t} \tag{3}$$

was used. Where, ΔW is the weight difference in milligram; t is the exposure time in hours.

RESULTS AND DISCUSSION

Figure 1-5 show the graph of the deposited film thickness (mg cm^{-2}) against exposure time (h) for various Al-Zn alloys in various molar concentrations of brine; while Fig. 6-10 show deposition rate (mg s^{-1}) against exposure time (h) for various Al-Zn alloys in various molar concentrations of brine.

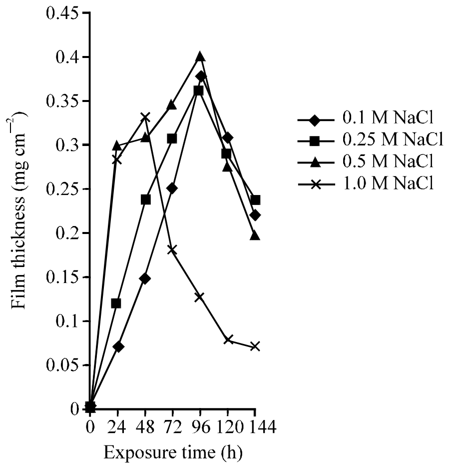

Fig. 1: Deposited film thickness (mg cm^{-2}) against exposure time (h) for Al-1.0% Zn in various molar concentrations of brine

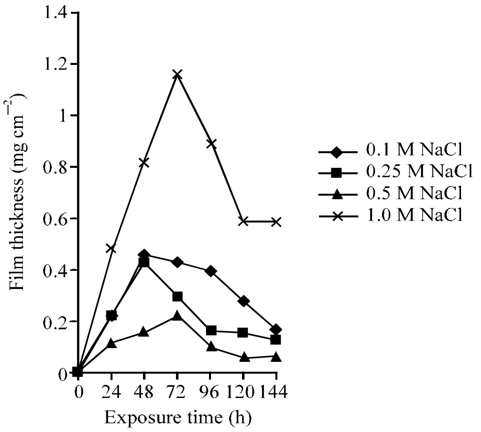

Fig. 2: Deposited film thickness (mg cm^{-2}) against exposure time (h) for Al-2.0% Zn in various molar concentrations of brine

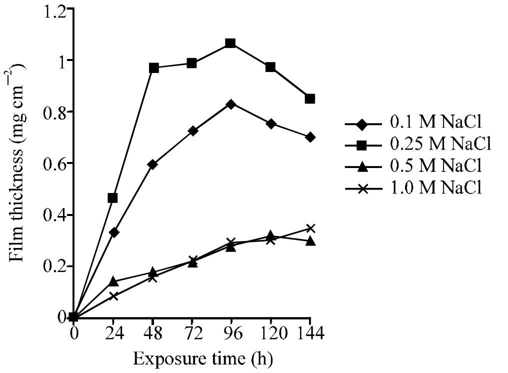

Fig. 3: Deposited film thickness (mg cm^{-2}) against exposure time (h) for Al-2.5% Zn in various molar concentrations of brine

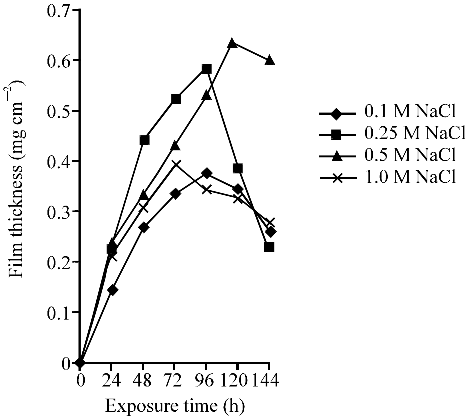

Fig. 4: Deposited film thickness (mg cm^{-2}) against exposure time (h) for Al-3.5% Zn in various molar concentrations of brine

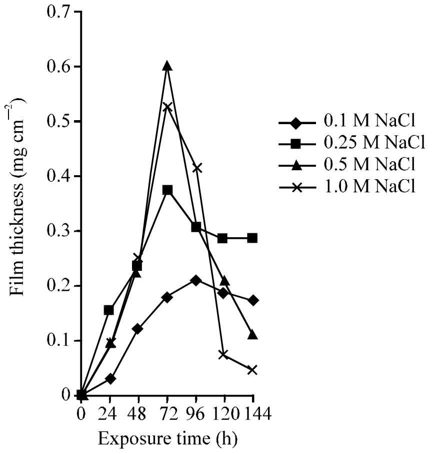

Fig. 5: Deposited film thickness (mg cm^{-2}) against exposure time (h) for Al-4.0% Zn in various molar concentrations of brine

Deposited Thin film Thickness

The scale film thickness is unavoidably a good index for passivation characterization especially as passivation phenomenon basically is statistical in nature hence, offering an insight into what really happens to materials in a passivating environment. The formation of thin protective layers at metals, which could be successfully used for corrosion control, has long been the focus of attention for corrosion experts. Those layers are formed either during the adsorption of corrosion inhibitors (CIs) or in reactions of the cations of the metal to be protected with some components of the medium. The latter case involves not only nanosized layers formed by CIs but also thick conversion (oxide, phosphate, etc.) coatings (Kuznetsov, 2006). It can be inferred from Fig. 1-5 that there is an initial rapid increase on adsorption rate of the scale films on the surface of the test samples which peaked at the range of 48-72 h exposure time before progressively declining in all the alloy compositions in the various test environments, a phenomenon attributed to the nature of the adsorbing surface consequent upon the ion mobility which depends on the media saturation. The varying stability points of the adsorbed layers (deposited film thickness) in the various simulated enviroumeuts may be due to the nature of the adsorbing surface as a result of the concentration of the test environments. A perusal at Fig. 1-5 show that the calculated passivated layers (deposited scale film) was in agreement with the layer thickness of scale films which is in the order of nanometer (10^{-9}). When compared however, the brine concentration in the range 0.25 to 0.5 M showed the greatest deposited layer thickness in the entire test enviroumeuts, which increased with increase in exposure time. This behaviour is possibly attributable to the fact that maximnm deposition apparently occurs at about this range due to increased electrical conductivity predicated on the increased oxygen solubility, which occurred within this range but progressively declined due to immobility of current carrying ions.

Scale Film Deposition Rate

The scale film deposition rate has imbedded in it the important property of the rate at which adsorption of corrosion products occurs on the surface of any passivating material subjected to simulated corrosive environments. From Fig. 6-10, it can be inferred that the deposition rate correlates well with the observed deposited scale film thickness earlier discussed. It increased albeit exponentially

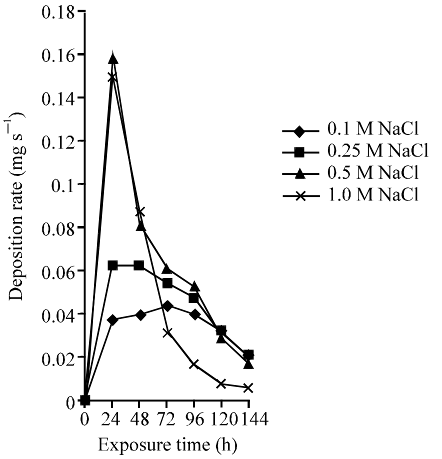

Fig. 6: Deposition rate (mg s^{-1}) against exposure time (h) for Al-1.0% Zn in various molar concentrations of brine

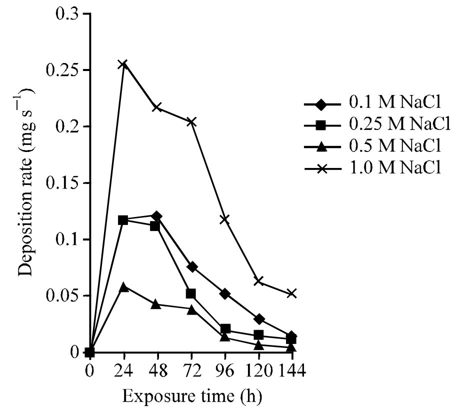

Fig. 7: Deposition rate (mg s^{-1}) against exposure time (h) for Al-2.0% Zn in various molar concentrations of brine

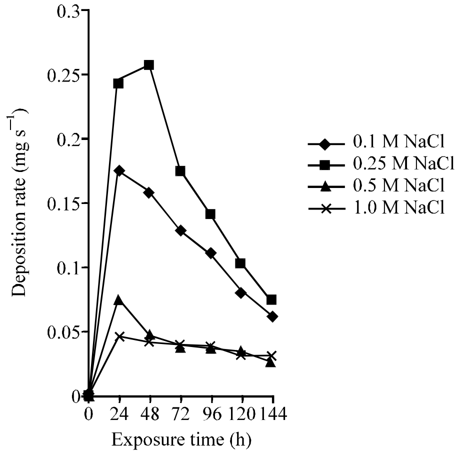

Fig. 8: Deposition rate (mg s^{-1}) against exposure time (h) for Al-2.5% Zn in various molar concentrations of brine

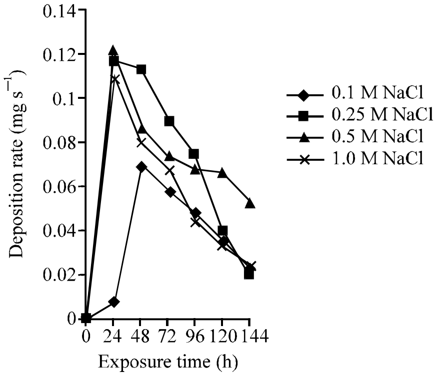

Fig. 9: Deposition rate (mg s^{-1}) against exposure time (h) for Al-3.5% Zn in various molar concentrations of brine

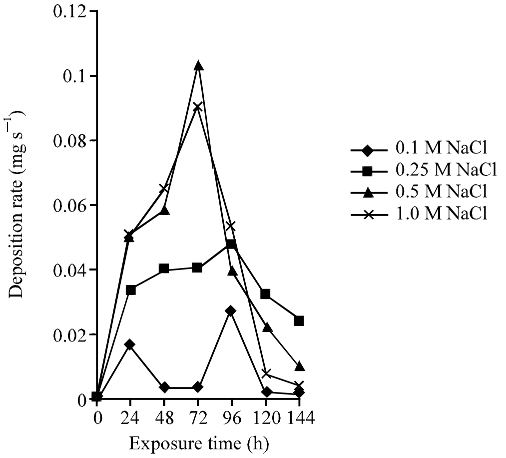

Fig. 10: Deposition rate (mg s^{-1}) against exposure time (h) for Al-4.0% Zn in various molar concentrations of brine

with exposure time peaking at the average exposure time of 24 h before gradually declining due to the saturation of the media concentration at this point. Hence, with increasing salt concentration, scale film deposition rate will initially increase due to increasing electrical conductivity, while at higher salt concentration; the scale film deposition rate will decline, owing to the decrease in the solubility and diffusion rate of oxygen.

CONCLUSION

The analysis has shown that passivation phenomenon is a consequence of media concentration. The presence of the aggressive ion chloride in the corrosive environment indeed does contribute to the passivation characteristics of materials as evidently can be seen from all the figures. The observed increased passivation kinetics in the brine media concentration range of 0.25 to 0.5 M significantly indicates that seawater environment (0.3 M NaCl) is in good standing for habouring Al-Zn alloys as this range portrays the region of maximum adsorption.

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