Nigerian Journal of Technology (NIJOTECH)
Vol. 34 No. 4, October 2015, pp. **705 – 709**

ISSN: 0331-8443
www.nijotech.com
http://dx.doi.org/10.4314/njt.v34i4.6

EFFECT OF PRE-AGEING THERMAL CONDITIONS ON THE CORROSION PROPERTIES OF ANTIMONY-MODIFIED Al-Si-Mg ALLOY

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ABSTRACT
The purpose of this investigation was to evaluate the effect of pre-ageing thermal conditions on the corrosion properties of antimony-modified Al-Si-Mg alloy.The alloy was subjected to a Single Thermal Ageing Treatment; STAT (T6 temper-solution heat treatment and ageing) and Double thermal ageing treatment; DTAT (T7 temper-solution heat treatment and ageing for stabilization). These consist of solution heat treatment (SHT) at 540^oC for 1hr, water quenched followed by an artificial ageing; DTAT and STAT. For the single thermal ageing treatment (STAT), quenched samples were aged at temperatures of 180^0C for 2hrs, before cooling in air. In the double thermal ageing treatment (DTAT), quenched samples were pre-aged at a temperature of 90^oC, 105^oC and 120^oC for 1- 5 hrs. This was followed by ageing at 180^oC for 2hrs before cooling in air. The corrosion characteristic of the as-cast, Single Thermal Ageing Treatment (STAT) and Double Thermal Ageing Treatment (DTAT) were evaluated using weight loss and linear polarization techniques in a static 3.5%NaCl solution. From the results, the corrosion rate decreases with increasing pre-ageing time and temperatures. Equally, from the linear polarization data/curves, the corrosion rate of the treated alloy decreases at all ageing temperatures along with the ageing time. The Optical Microscope (OM) results of as-corroded samples revealed that the alloy suffers pitting/uniform corrosion. The corrosion behaviour of the DTAT samples in simulated seawater showed an excellent improvement in corrosion resistance than the as-cast and conventional STAT alloy.

Keywords: *Al-Si-Mg alloy, thermal ageing, polarization, eutectics, interdendritic spacing.*

1. INTRODUCTION

Corrosion of aluminium alloys lead to impairment of its operation and progressive weakening of that structure. The consequences of corrosion are many, and its effects on safety, reliability, and efficiency in structural operations are often considered than simply loosing of a volume of metal. Various kinds of failures and the need of expensive replacements may occur even though the amount of metal destroyed is quite small. One of the major harmful effects of corrosion is the reduction of metal thickness leading to loss of mechanical strength and structural failure, causing serious disasters and risk to the life of people.

Deep pitting corrosion arises in aluminum alloys when there is a long-term effect from aggressive water containing chloride (e.g. seawater). Beside the chloride content, the amount of oxygen in the water also plays a role; corrosion reaction can only occur in neutral media (pH = 4.5-8.5) in the presence of oxygen [1]. The remedy for this can come in the form of passive protection by coating or by means of active cathodic corrosion protection using a sacrificial anode, for example. Magnesium as an alloying element causes the formation of a thicker oxide layer containing magnesium oxide (MgO). Equally, it consequently provides greater corrosion protection against water containing chlorides and slightly alkaline media (e.g. ammonia solutions). This is because magnesium oxide in contrast to aluminium oxide is insoluble in alkaline solutions. However, Al-Si-Mg alloys are groups of heat treatable cast Al-Si alloys [2,3], which after fabrication, needs an artificially aging heat treatment to attain the desired strength [4,5].The alloys have a wide range of applications in the automobile and aerospace, defense and general engineering industries[6]. A356 (Al-7Si-0.3Mg) and A357 (Al-7Si-0.5Mg) series are the two

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commonly used Al-Si-Mg alloys [7] used to obtain near neat shape products [8] because of its high fluidity and good castability [9], owing to the high volume of Al-Si eutectic, in the microstructure. In some previous studies, the effect of pre-ageing thermal treatment was conducted on a sodium modified Al-Si-Mg alloy with improved properties [10, 11]. The purpose of this investigation was to evaluate the effect of pre-ageing thermal conditions on the corrosion properties of antimony modified Al-Si-Mg alloy.

2. EXPERIMENTAL PROCEDURE

2.1. Sample Preparation and Experimental Techniques

The Al-Si-Mg alloy with the chemical composition as shown in Table 1, were smelted in Alumina crucible. The smelting was done using a muffle resistance furnace that was allowed to heat to 750^{o}C, the crucible was removed and other alloying elements added. The crucible was then returned to the furnace to heat for 30minutes during which the temperature of the melt was raised to 800^{o}C, and then Mg was added (ladle addition) before pouring into the mould. The eutectics silicon particles were modified with antimony (0.01%). The alloy was subjected to a Single Thermal Ageing Treatment; STAT (T6 temper-solution heat treatment and ageing) and Double thermal ageing treatment; DTAT (T7 temper- solution heat treatment and ageing for stabilization). These consist of solution heat treatment (SHT) at 540^{o}C for 1hr, water quenched followed by an artificial ageing; DTAT and STAT. For the single thermal ageing treatment (STAT), quenched samples were aged at temperatures of 180^{0}C for 2hrs, before cooling in air. In the double thermal ageing treatment (DTAT), quenched samples were pre-aged at a temperature of 90^{o}C, 105^{o}C and 120^{o}C for 1 – 5hrs. This was followed by ageing at 180^{o}C for 2hrs before cooling in air. The samples for microstructural examination using OPM and SEM were electro-polished and etched with Keller's reagent (190ml H_2O+5ml NHO_3 + 3ml HCl + 2ml HF).

Table 1: Chemical Composition of the produced Al-Si-Mg Alloy (wt %)

Al	Si	Mg	Mn	Cu	Fe	Ti	Zn	Sb
92.92	6.5	0.35	0.03	0.03	0.08	0.05	0.03	0.01

2.2. Weight Loss Technique

The weight loss technique was used to characterize the corrosion rate of 340 samples comprised As-cast, STAT and DTAT samples. Sets of same concentration of 3.5 NaCl in 100ml were prepared (for the As-cast and heat treated). The coupons were cleaned before suspended in the static 3.5%NaCl solution with the aid of threads.

Weight losses of the coupons were taken at intervals of two days (48hrs) over a period of forty days (960hrs). After removing the coupons from the solution, the surfaces were then scrubbed with brush in distilled water, rinsed in ethanol and air dried for weighing.

2.3. Linear Polarization Technique

A total of seventeen (17) samples which comprised As-cast, STAT and DTAT samples were subjected to linear polarization technique to characterize the corrosion rate (current density), that consist cyclic scan, employing the linear polarization technique. A potentiostat coupled to a computer system, a glass corrosion cell kit with graphite rods as counter electrodes and a saturated Ag/Ag reference electrode were used. The working electrodes were the alloy samples. The samples were positioned at the glass corrosion cell kit, leaving a 3.808 cm^2 alloy surface in contact with the solution. Polarization test were carried out in 3.5wt% NaCl solution at room temperature in a static solution for a period of 30 minutes using a potentiostat. The polarization curves were determined by stepping the potential at a scan rate of 0.0016V/sec. The polarization curves were plotted using Autolab data acquisition system (Autolab model: Aut71791 and PGSTAT 30), and both corrosion rate and potential were estimated by the Tafel extrapolation method (corrosion rate analysis) using the anodic and cathodic branches of the polarization curves.

3. RESULTS AND DISCUSSION

3.1 Corrosion Techniques

The corrosion rate data of Al-Si-Mg alloy in 3.5wt% NaCl results are shown in Tables 2-4 with evidence that the double thermal ageing treatment (DTAT) improved the corrosion resistance compared to the convectional single thermal ageing treatment (STAT).The corrosion resistance of DTAT at 90^{o}C decreases with ageing time except at 4hrs, which shows an appreciable improvement than the 3hrs aged samples. At 105^{o}C, the corrosion resistance decreases with ageing time but, at 120^{o}C the 2hrs ageing time has a higher corrosion resistance than the 1hr ageing time. The potentiodynamic scanning curves and the corresponding corrosion parameters of As-cast, STAT and DTAT for A356.0-type Al-Si-Mg alloy in a 3.5wt% NaCl were generated from the potentiostat with the view to improve the corrosion resistance of the alloy in a novel double thermal ageing treatment. The corrosion rate of all the samples studied showed a smaller passive region (cathodic) and prolong active region (anodic). Observations from the results indicated that the corrosion rates are very similar in trend for all the examined samples irrespective of the treatment. This is because the samples were from the same alloy which was cast and solidified in similar conditions and cooling rate. However, the corrosion rate increases with increasing ageing time (Figures 1-3) for all the DTAT samples. This is in agreement to those reported in literature [12, 13, 14].

Table 2: Linear polarization data of thermally aged Al-Si-Mg alloy at 90^{0}C in 3.5%NaCl solution

Samples	Jcorr (A/cm²)	icorr (A)	Corrosion rate (mm/year)	Polarization resistance (Ω)
As-received	2.03E-03	7.72E-03	22.814	18.780
180/2hr	4.18E-04	1.59E-03	4.6947	71.929
90/1hr	2.67E-09	1.02E-08	3.00E-05	5.52E+07
90/2hr	3.62E-06	1.38E-05	4.069E-02	8572.5
90/3hr	1.94E-05	7.36E-05	2.175E-01	3694.4
90/4hr	3.09E-05	1.17E-04	3.471E-01	562.33
90/5hr	6.28E-05	2.39E-04	7.056E-01	772.37

Table 3: Linear polarization data of thermally aged Al-Si-Mg alloy at 105^{0}C in 3.5%NaCl solution

Samples	jcorr (A/cm²)	icorr (A)	Corrosion rate (mm/year)	Polarization resistance (Ω)
As-received	2.03E-03	7.72E-03	2.2814E+01	1.8780E+01
r	4.18E-04	1.59E-03	4.6947	7.1929E+01
105/1hr	1.13E-09	4.29E-09	4.36E-06	3.30E+07
105/2hr	4.68E-07	1.78E-06	5.265E-03	1.4409E+04
105/3hr	7.56E-06	2.87E-05	8.496E-02	1.8871E+03
105/4hr	9.69E-06	3.69E-05	1.089E-01	1.2686E+03
105/5hr	9.76E-05	3.71E-04	1.0971	2.0633E+02

Table 4: Linear polarization data of the thermally aged Al-Si Mg alloy at 120^{0}C in 3.5% NaCl solution

Samples	Jcorr-(A/Cm²)	Jcorr-(A)	Corrosion rate (mm/year)	Polarization resistance (Ω)
As received	2.03E - 03	7.72E-03	22.814	18.780
180/2hr	4.18E - 04	1.59E-03	4.6947	71.929
120/1hr	6.09E - 07	2.31E-06	6.84E-03	2576.6
120/2hr	5.18E - 06	1.97E-05	5.825E-02	6867.5
120/3hr	1.37E - 05	5.23E-05	1.545E-01	3687.1
120/4hr	6.34E - 05	2.41E-04	7.131E-01	1360.4
120/5hr	1.53E-04	5.8E-04	1.7142	106.76

It can be clearly seen that the corrosion potential at 90^{o}C/5hrs is the most positive and same with those of as-cast and STAT samples, while that at 90^{o}C/1hr is the most negative (Table 3 and Figure 1). Similarly, the value of the polarization Resistance (Rp) at 105^{o}C/1hrs is the highest (Table 2). Corrosion rate of the sample pre-aged at 120^{o}C was reduced (Table 3 and Figure 3), though higher than those obtained at 90^{o}C and 105^{o}C temperatures. These results indicated that the particles of aluminum alloyA356-type at STAT condition are more susceptible to corrosion than DTAT at all ageing temperatures and time; because of it low polarization potential and current density when compared to that of DTAT. Figures 1-3 show the current densities (corrosion rate) and their corresponding corrosion potential at 90^{o}C, 105^{o}C and 120^{o}C respectively. The ageing temperatures and the degree of super saturation played a major role in the final properties of the alloy. However, as the ageing progresses, the inter-atomic spacing and the bond between the molecules changed which accounts for the electrochemical behavior of these samples. Such tendency agreed with the results obtained elsewhere [12, 14]. The corrosion resistance of A356.0-type Al-Si-Mg alloy studied seems to be strongly associated not only with the distribution of eutectics which is dependent on the interdendritic spacing, but also with the fineness of the eutectic inter-phase spacing. These are in par with the works of [15] and [16]. Comparatively, samples aged at 105^{0}C for 1hr at DTAT exhibit the highest corrosion resistance in 3.5wt% NaCl solution considered in this work both in weight loss and linear polarization techniques employed.

3.2 Microstructure and degradation of Al-Si-Mg alloy after electrochemical corrosion attack

Plates Ia and Ib are the as-cast microstructures of Al-Si-Mg alloy without and with antimony modification respectively. The as-cast shows the presence of few pits in a uniformly corroded pattern at the 20th day (Plate IIa). A uniformly corroded sample was obtained with deep pits at the 30th day while many deeper pits were observed on 40th day of exposure (Plates IIb, IIc).

4. CONCLUSIONS

The results from the weight loss of Al-Si-Mg alloy in static 3.5%NaCl solution at 298K has shown that the corrosion resistance of DTAT Al-Si-Mg alloy has been enhanced significantly as compared to those observed in the STAT condition. The results of the linear polarization indicated that DTAT treatment has greatly improved the corrosion resistance of samples at all the pre-ageing temperatures and time as compared with the STAT tempers condition.

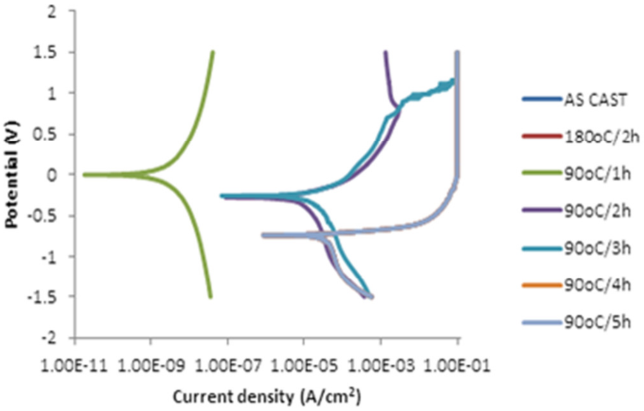

Figure 1: Linear polarization of thermally pre-aged Al-Si-Mg alloy at 90°C in 3.5%NaCl solution at 298K.

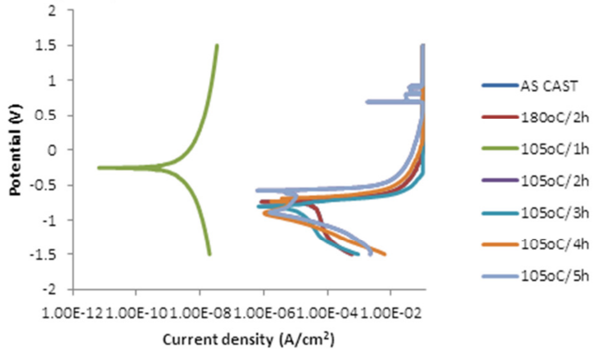

Figure 2: Linear polarization of thermally pre-aged Al-Si-Mg alloy at 105°C in 3.5%NaCl solution at 298K.

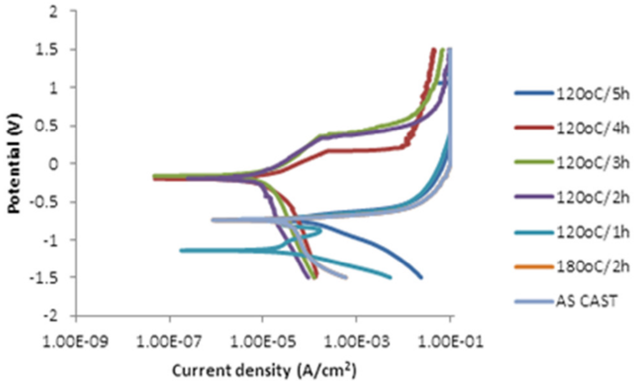

Figure 3: Linear polarization of thermally pre-aged Al-Si-Mg alloy at 120°C in 3.5%NaCl solution at 298K.

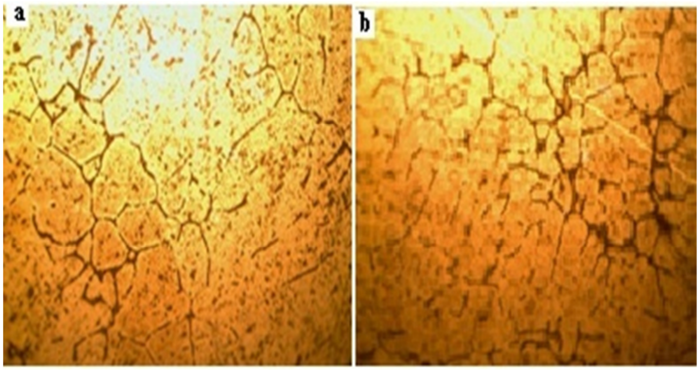

Plate I: Optical microstructure of (a.) as-cast structure (b.) Antimony modified Al-Si-Mg alloy

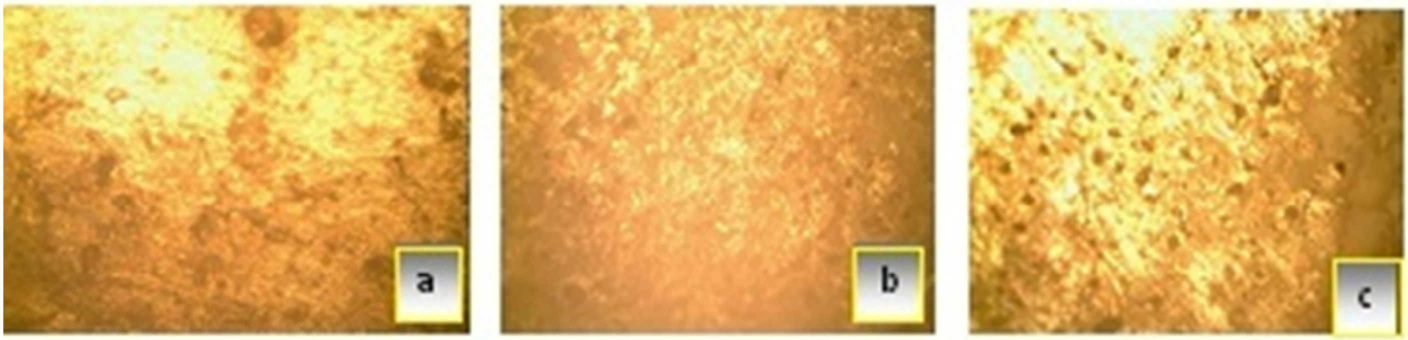

Plate II: OPM of (a.) as cast in the as corroded at 20th day (b.) as-corroded at 30th day (c.) as-corroded at 40th day.

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