

## **Degradation Behavior of High Chromium Sodium-Modified A356.0-Type Al-Si-Mg Alloy in Simulated Seawater Environment**

**M. Abdulwahab<sup>\*1,2</sup>, I.A. Madugu<sup>1</sup>, S.A. Yaro<sup>1</sup>, A.P.I. Popoola<sup>2</sup>**

<sup>1</sup>Department of Metallurgical and Materials Engineering, Ahmadu Bello University, Zaria,  
Nigeria

<sup>2</sup>Department of Chemical and Metallurgical Engineering, Tshwane University of Technology,  
Pretoria, Republic of South Africa

\*Corresponding Author: mabdulwahab@abu.edu.ng

### **ABSTRACT**

*The effect of multiple-step thermal ageing treatment (MSTAT) on the corrosion characteristics of A356.0-type Al-Si-Mg alloy in simulated seawater has been studied. The MSTAT treatment also consists of Double Thermal Ageing (DTAT- T7), Single Thermal Ageing (STAT- T6), Step-Quenching and Ageing (SQA). The corrosion of the thermal treated samples was characterized by electrochemical Potentiodynamics polarization techniques consisting of linear polarization and chronopotentiometric method using the fit Tafel plot. Generally, from the linear polarization, the corrosion rate decreases at all temperatures with the ageing time. The corrosion behavior of the DTAT and SQA Al-Si-Mg alloy in the simulated seawater showed better resistance than the STAT Al-Si-Mg alloy. Samples in the SQA-STAT have improved corrosion resistance than the SQA-DTAT one. The chronopotentiometric corrosion study of some selected samples indicates a decrease in the corrosion resistance with open circuit potential exposure time. Consequently, the form of corrosion in the studied Al-Si-Mg alloy are slightly uniform and predominantly pitting corrosion as obtained from the SEM study. The pits diameter were found to range from 30-50µm.*

**Key words:** pits diameter, MSTAT, degradation behavior, corrosion rate.

### **1. INTRODUCTION**

Foundry aluminium alloys based on the Al-Si system are widely used in the automobile field since they provide excellent fluidity and castability, good resistance to corrosion and mechanical

properties [1-4]. Al-Si alloys are characterized by a wide temperature range in the semi-solid region [1,5]. Al-Si alloys, which comprise 85% to 90% of the total aluminium cast parts produced, exhibit excellent castability, mechanical and physical properties [6,7]. Aluminium alloys has successfully penetrated the automotive market, largely (> 75%) in the form of castings [8]. Addition of Mg to Al-Si (A356 alloys) is the main solid solution strengthener to aluminium alloys and responsible to precipitation hardening (PH) to yield higher strength [9-12]. A356 alloys contains silicon but also magnesium as main alloying elements. It shows response to heat treatment [1,3,13-16] and increase strength by precipitation of  $Mg_2Si$  in aluminium matrix [1,17-24].

Aluminium and its alloys are considered to be highly corrosion resistant under the majority of available service condition [25]. The various grades of pure aluminium are most resistance, followed closely by the Al-Mg, Al-Mn alloys. Next in order is Al-Mg-Si and then Al-Si alloy. The alloy containing copper are the least resistant to corrosion; but this can be improved by coating each side of the copper containing alloy with a thin layer of high purity aluminium, thus gaining a three ply metal, i.e. Alclad. This cladding acts as a mechanical shield and also protects the material by sacrificial [26]. When aluminium surface are exposed to the atmosphere, a thin invisible oxide ( $Al_2O_3$ ) skin forms, which protects the metal from corrosion in many environments [25]. This film protect the metal from further oxidation unless this coating is destroyed, the material remains fully protected against corrosion [27,28]. The composition of an alloy and its thermal treatment are of important for susceptibility of alloys to corrosion [29].

In the development and processing of aluminium alloys, various works have been reported on the degradation of the alloys at various environment and operating conditions. Several methods of controlling and preventing or minimizing corrosion attack in aluminium alloys have been demonstrated by different authors. Alloying addition have been reported to successfully reduced corrosion attack in aluminium alloy [30,31]. Other methods of corrosion control include inhibitors addition [32-34]. Heat treatment (PH) (including DTAT) [31,35-40]. Corrosion resistance of Al-Si-Mg alloy is much better than the aluminium-copper alloys [41]. On the microstructural and submicroscopic scales, the electrochemical properties develop point-to-point non-uniformities that account for changes in resistance of the alloy [42]. Abdulrahman and Agbodion [43] studied the effect of ageing time and temper on the corrosion of Al-Si-Cu alloy in varying HCl concentrated acid solution. They noticed that the rate of corrosion of the alloy increased with increase in concentrations of the acid and decreased sharply with time.

Khoshnaw and Gardi [44] studied the effect of ageing time and temperature on exfoliation corrosion of aluminium alloys 2024-T3 and 7075-T6. They observed that with increase in the ageing time for aluminium alloy type 2024-T3, the susceptibility to exfoliation corrosion increase while for the 7075-T6 decreased. The intermetallic compounds formed such as  $CuAl_2$  and  $MZn_2$  phase increase with increase in ageing time for both alloys. Aluminium alloys has

been used for along time because of it essential properties. New demanding applications are developed continuously. To be able to make the alloys competitive in future applications, assess to powerful tools and methods for materials or/ properties development is essential. The interest in this work for DTAT and SQA treatments comes from the possibility to improve the corrosion resistance of Al-Si-Mg alloy in the T6 temper. It is on this note that an electrochemical corrosion test consisting of linear polarization and chronopotentiometric as a means of corrosion assessment of this group of alloy was carried out after these novel thermal treatments.

## 2. MATERIALS AND METHODS

The A356.0-type Al-Si-Mg alloy with chemical composition (see Table 1) was produced according to the methods described elsewhere [30,45]. Some seconds to pouring of the molten alloy into the mould, 0.01% elemental sodium was added and stirred thoroughly. The cast samples were machined to specified electrochemical corrosion dimensions at the Centre for Advanced Manufacturing Technology (CAMT), Tshwane University of Technology, Soshanguve, Pretoria, Republic of South Africa.

Table 1. Chemical composition of the produced A356.0-type Al-Si-Mg alloy (wt %).

Al	Si	Mg	Fe	Mn	Cr	Pb+Sn	Zn	Cu	Ti	Ni	Na
92.14	7.00	0.30	0.08	0.03	0.20	0.03	0.05	0.03	0.11	0.03	0.01

The electrochemical potentiodynamics technique was used to characterize the corrosion rate (current densities) consisting of linear polarization and chronopotentiometric or open circuit potential (OCP). A potentiostat coupled to a computer system, a glass corrosion cell kit with a platinum counter electrode and a saturated Ag/Ag reference electrode were used. The working electrodes consist of thermally aged alloys. The samples were positioned at the glass corrosion cell kit, leaving a 3.803cm<sup>2</sup> alloy surfaces in contact with the solution. Polarization test were carried out in a 3.5wt%NaCl solution at room temperature (RT) using a potentiostat. The polarization curves were determined by stepping the potential at a scan rate of 0.003V/sec. The polarization curves were plotted using Autolab data acquisition system (Autolab model: AuT71791 and PGSTAT 30), and both the corrosion rate and potential were estimated by the Tafel extrapolation method (Tafel plot or corrosion rate analysis) using both the anodic and cathodic branches of the polarization curves. The chronopotentiometric (OCP) was also used to assess the corrosion behavior of some alloys samples in order to determine whether there was prolong or short passive or active condition. The electrochemical corrosion test was done at Department of Chemical and Metallurgical Engineering, Tshwane University of Technology, Pretoria, Republic of South Africa.

### 3. RESULTS AND DISCUSSIONS

#### 3.1 Results

The corrosion rate analysis from the linear polarizations using the data from the Tafel plots have been represented in the normal form; shown as Figures 1-6 and the OCP curves are presented as Figure 7. The SEM of the surface morphology of some treated as-corroded samples can be found in Plates 1-5.

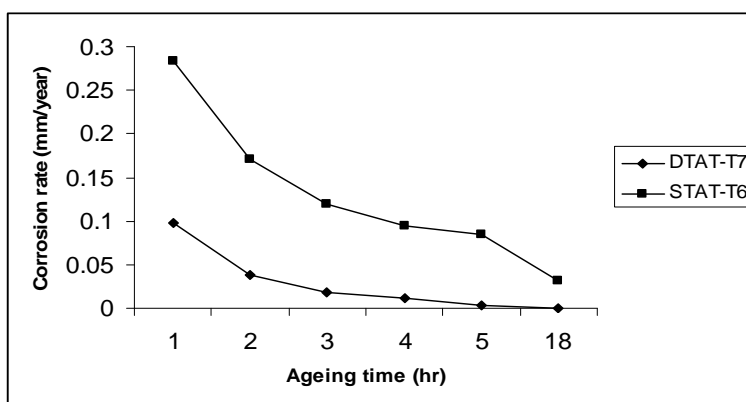


Figure 1: Variation of corrosion rate with ageing time for DTAT-T7 and STAT-T6 A356.0-type Al-Si-Mg alloy at 150°C from the Tafel plot data in simulated seawater environment.

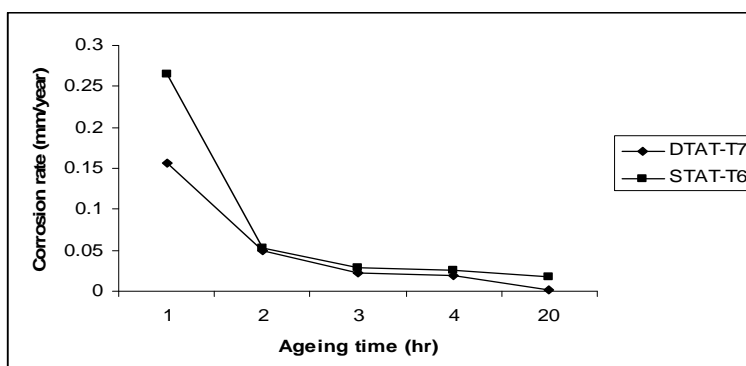


Figure 2: Variation of corrosion rate with ageing time for DTAT-T7 and STAT-T6 A356.0-type Al-Si-Mg alloy at 180°C from the Tafel plot data in simulated seawater environment.

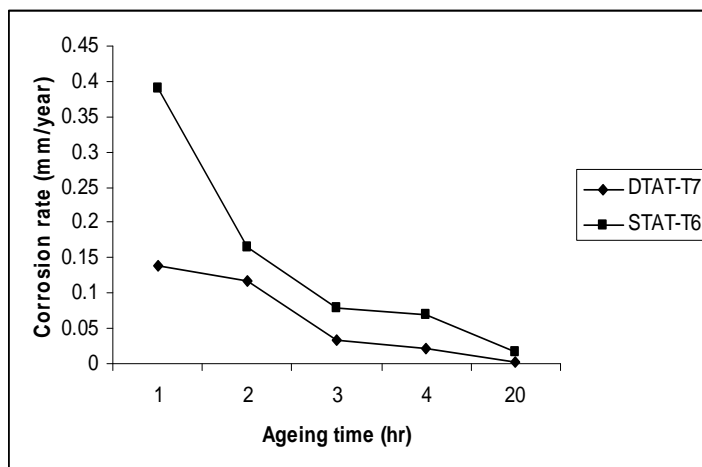


Figure 3: Variation of corrosion rate with ageing time for DTAT-T7 and STAT-T6 A356.0-type Al-Si-Mg alloy at 210°C from the Tafel plot data in simulated seawater environment.

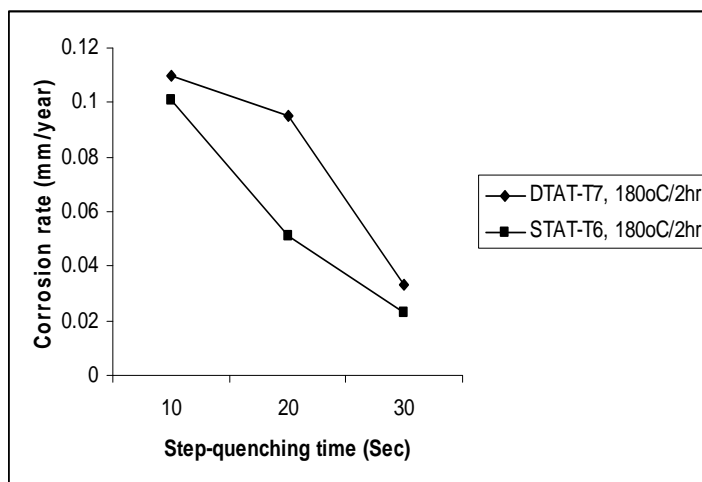


Figure 4: Variation of corrosion rate with ageing time for DTAT-T7 and STAT-T6 A356.0-type Al-Si-Mg alloy at 220°C SQ temperature and aged 180°C/2hr from the Tafel plot in simulated seawater environment.

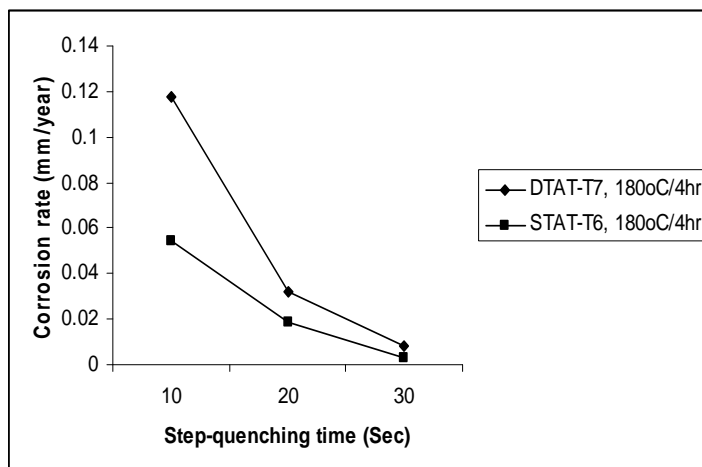


Figure 5: Variation of corrosion rate with ageing time for DTAT-T7 and STAT-T6 A356.0-type Al-Si-Mg alloy at 220°C SQ temperature and aged at 180°C/4hr from the Tafel plot in simulated seawater environment.

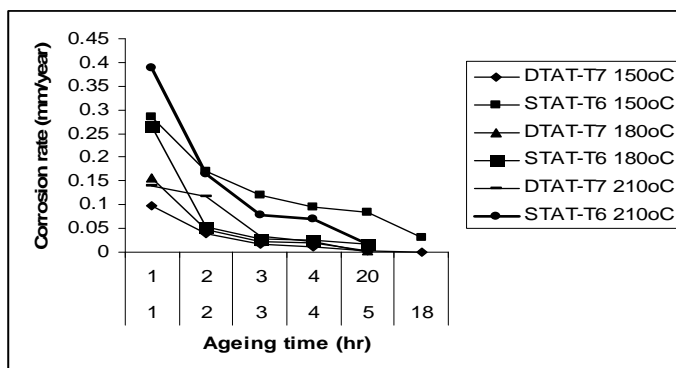


Figure 6: Comparative study of corrosion rate for DTAT-T7 and STAT-T6 A356.0-type Al-Si-Mg alloy at 150°C, 180°C and 210°C at various ageing time from the Tafel plot data in simulated Seawater environment

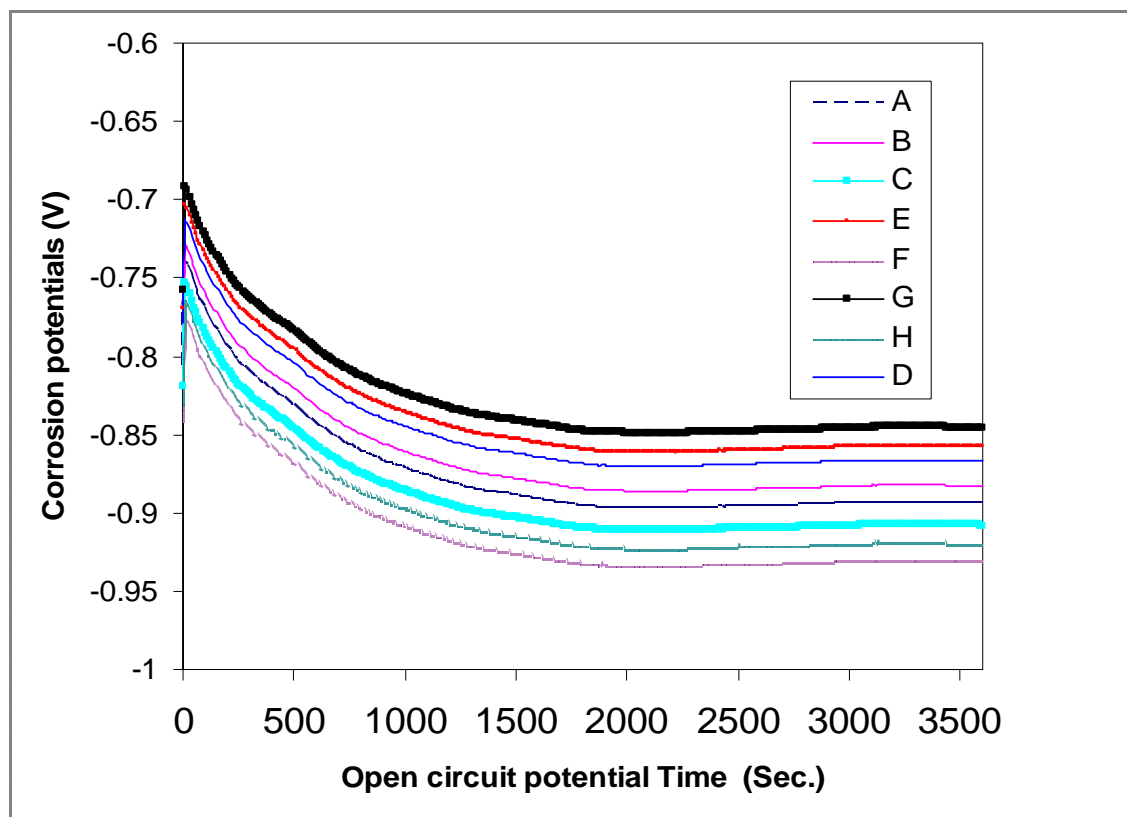


Figure 7: Chronopotentiometric curve for some selected DTAT and STAT A356.0-type alloys (A) STAT-T6 150°C/18hr (B) STAT-T6, 180°C/20hr (C) STAT-T6, 210°C/20hr (D) DTAT-T7, 180°C/20hr (E) DTAT-T7 210°C/20hr (F) SQA DTAT-T7, 220°C/30sec., 180°C/4hr (G) DTAT-T7 150°C/18hr (H) SQA STAT-T6, 220°C/30sec., 180°C/4hr

## 3.2 Discussion of Results

### 3.2.1 Corrosion characteristics

#### 3.2.1.1 Potentiodynamics linear polarization and MSTAT treatment

From Figures 1-6, the potentiodynamics polarization curves for A356.0-type Al-Si-Mg alloy subjected to different MSTAT treatment in a 3.5wt% NaCl are presented. However, the corrosion rate decreases with increasing ageing time (see Figures 1-6) for all the DTAT, STAT, SQA; DTAT and STAT samples considered. This is in agreement to those reported [43,44,46-49]. The corrosion rate of DTAT and STAT samples at 150°C, 180°C and 210°C decreases with increasing ageing time (1-20hr). The DTAT treatment has demonstrated a remarkable decrease in the corrosion rate than STAT samples at all ageing time. For example, at 150°C/1hr DTAT and STAT, the corrosion rates are 0.09766 and 0.284mm/year respectively. While at 18hr same

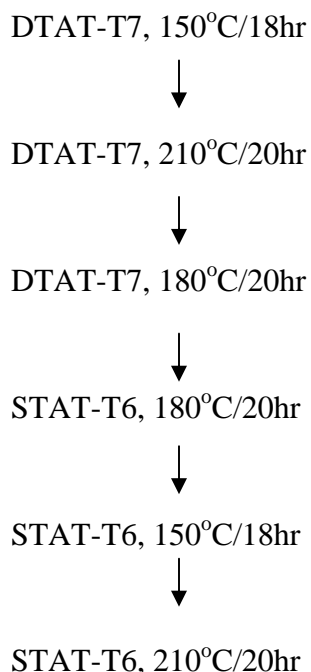
temperature, DTAT and STAT corrosion rates are 0.0002171 and 0.03093mm/year respectively. However, similar results [50] and trends [48] have been reported. On the other hand, since the grain boundaries are often more susceptible to corrosion than the grain interiors because of the microstructural heterogeneity associated with grain boundaries [38,51,52]. It is expected that samples with higher have pronounced grain boundaries, as such higher hardness is expected for such sample. For all the DTAT samples investigated, the corrosion rate has been observed to be significantly lower than that obtained at the STAT condition for all ageing temperatures and time comparatively. One of the reasons for this behavior is that the pre-ageing treatment at 105°C/5hr in the DTAT is responsible for these decreases in the corrosion rate compare to those observed with the STAT samples. The phases formed which enhanced hardness may probably have some deleterious effect on the physicochemical properties of the alloy in the electrochemical polarization condition.

However, the SQA; DTAT-T7 at 180°C/2hr and 4hr have higher corrosion rate than those of SQA; STAT-T6 at 180°C/2hr and 4hr for all the step-quenching time considered (see figure 4 and 5). For example the current densities at SQA; DTAT-T7 at 180°C/2hr and 4hr (220°C/30sec.) are 2.031 and 0.5 $\mu\text{A}/\text{cm}^2$  as compared to those at SQA; STAT at 180°C/2hr and 4hr (220°C/30sec), the current densities are 1.419 and 0.1696 $\mu\text{A}/\text{cm}^2$  respectively. This results showed a very wide difference in the corrosion rate of the two conditions indicating that SQA; DTAT-T7 are more susceptible to corrosion attach than SQA; STAT-T6 samples within the studied conditions.

It is also believed that after quenching, particles of the second phase precipitates occurred which affect the physicochemical properties of the alloy. The ageing temperatures and the degree of supersaturation play 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 account for the electrochemical behavior of these samples. Such tendency agreed with the results obtained in previous study [29, 46]. The corrosion resistances 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.

Comparatively, samples aged at 150°C for 18hr at DTAT exhibit the highest corrosion resistance in 3.5wt%NaCl solution simulated environment considered in this work. The sequence below presents the decreasing order of corrosion resistance of the sample at various ageing temperature and time:





and

SQA 180°C/4hr; STAT-T6    → SQA 180°C/4hr; DTAT-T7    →  
 SQA 180°C/2hr; STAT-T6    → SQA 180°C/2hr; DTAT-T7.

The results above motivated the interest in examining the samples of best corrosion resistance at each ageing temperature considered using the chronopotentiometric analysis which enables the evaluation of the corrosion kinetic of the selected sample through corrosion potentials with prolong time.

### 3.2.1.2 Chronopotentiometric and MSTAT treatments

From the OCP study of the selected samples of higher corrosion resistance, the corrosion potential,  $E$  (V), decreases with the electrochemical exposure time (see Figure 7). This becomes stable (passive) throughout the study time. This shows that the resistances of the thermally treated alloy to corrosion attack decreases with increasing electrochemical exposure time and that the samples later developed passivity (protection against corrosion). At this 'stable-level', it is assumed that the sample has some level of passivity and immunity as a result of the corroding products which covers the corroding surface and retard/stabilizes corrosion attack. These observations have been reported [47,50]. It can also be observed, for example, that sample with highest corrosion resistance still have the best corrosion potential (T7150°C/18hr) indicating higher corrosion resistance in 3.5wt%NaCl solution.

### 3.2.2 Microstructures and degradation behavior after corrosion study of A356.0-type Al-Si-Mg alloy

The microstructure of some selected as-corroded samples after electrochemical corrosion study using SEM indicates some traces of cracks and pronounced pits; showing that the samples have suffered pitting corrosion attack (Plates 1-5). The exposure surface shows evidence of localized attack at the location of the intermetallic caused by the dissolution of the matrix. There was evidence of corroding products of intermetallic compounds in all the samples examined. Besides, several pits are visible in all samples examined at different magnifications; x300, x1000, x10000. In Plates 1 and 3 there seems to be uniform surface pits formations which are less deep as compared to those in Plates 2, 4 and 5. More pronounced deeper pit were seen in T6 150°C/3hr (Plate 4) and SQA T7 220°C/20sec.180°C/2hr (see Plate 5).

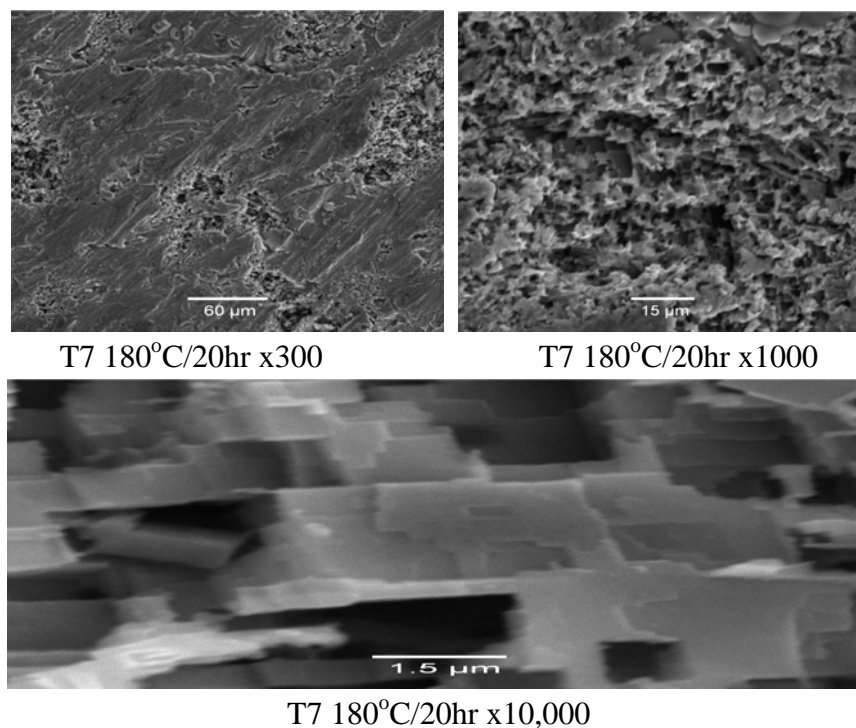


Plate 1: SEM Secondary Electron Image of the damaged surface Morphology of as- corroded T7 180/20hr in 3.5wt%NaCl Solution. Microstructures at different magnifications indicates several and severe pits.

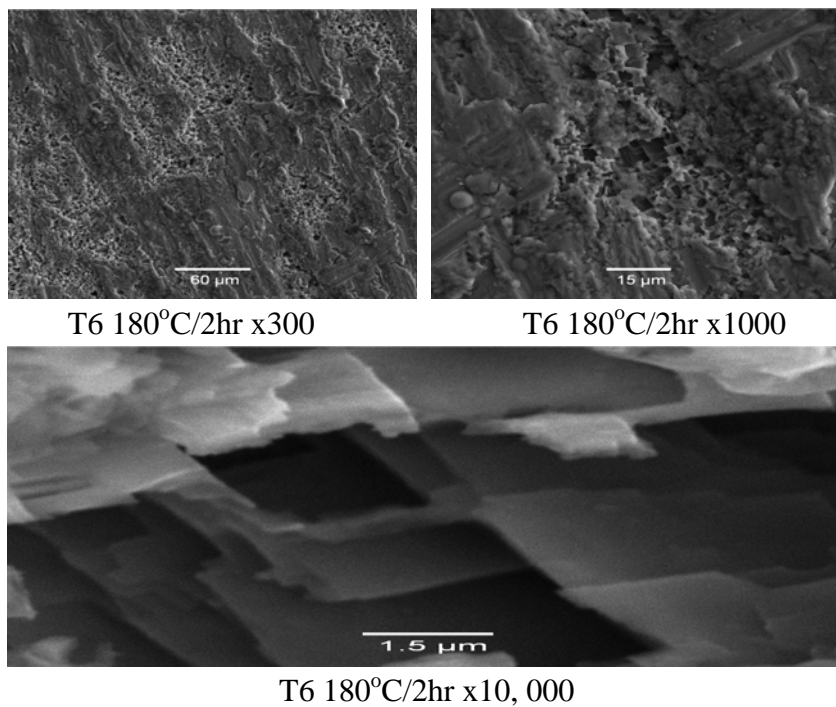


Plate 2: SEM Secondary Electron Image of the damaged surface Morphology of as-corroded T6 180/2hr in 3.5wt%NaCl Solution. Microstructures at different magnifications indicate several and severe pits higher than those observed in plate 10a.

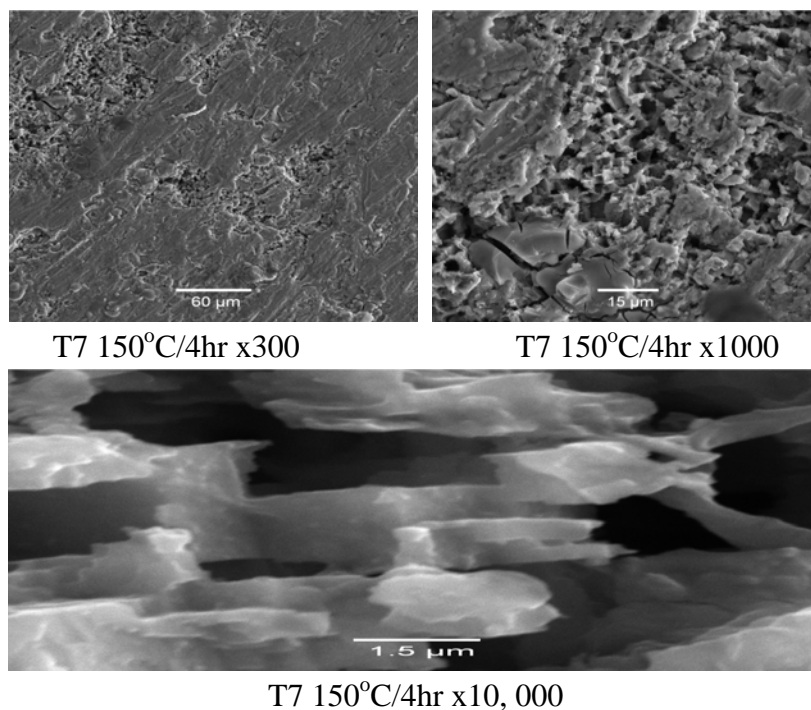


Plate 3: SEM Secondary Electron Image of the damaged surface Morphology of as-corroded T7 150/4hr in 3.5wt%NaCl Solution. Microstructures at different magnifications indicates several and severe pits. Indicating traces of cracks.

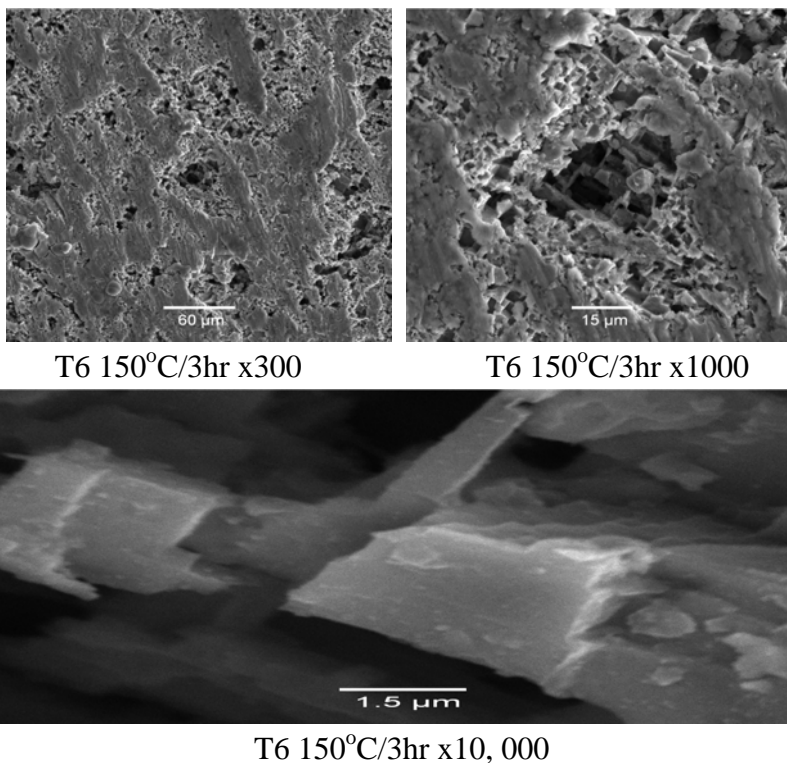


Plate 4: SEM Secondary Electron Image of the damage surface Morphology of as-corroded T6 150/3hr in 3.5wt% NaCl solution. Microstructures at different magnifications indicate severe pits deeper and wider than those observed in plate 10a, b, c.

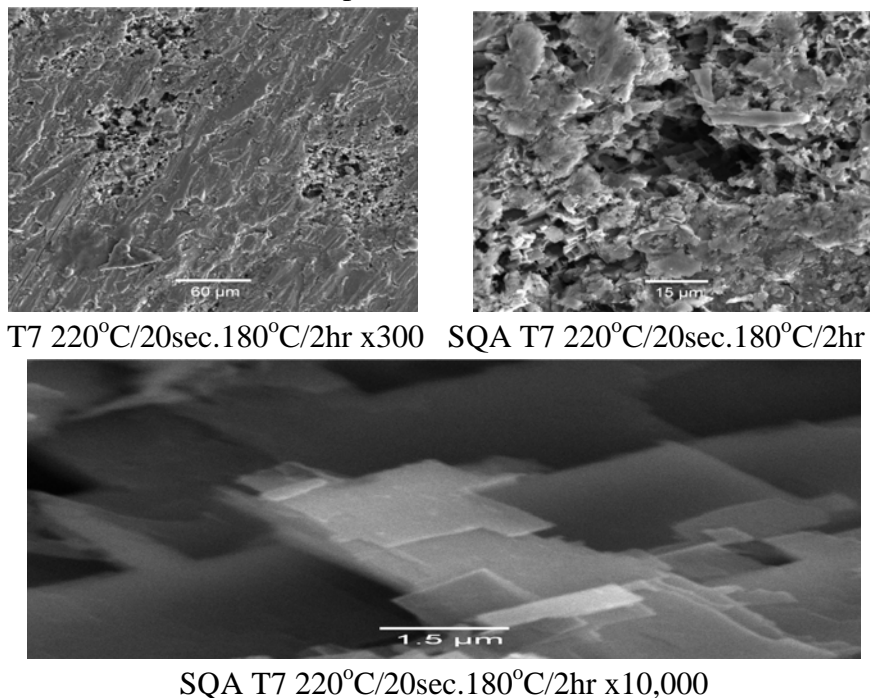


Plate 5: SEM Secondary Electron Image of the damaged surface Morphology of as-corroded SQA T7 220°C/20sec.180°C/2hr in 3.5wt% NaCl solution. Microstructures at different magnifications indicate severe pits deeper and wider than those observed in plate 10a, b, c.

The resultant pits diameter have been determined from the SEM surface morphology to range between 30-50 $\mu\text{m}$ . Specifically in T6 180°C/2hr (see Plate 2) the pit diameter are averages of 44.4445 and 50 $\mu\text{m}$ . It is probable that the pits are formed by intermetallic dropping out from the surface due to the dissolution of the surrounding matrix. However, it is also possible that the pits are caused by selective dissolution of the intermetallic/or particles of the second phase precipitates. Consequently, the form of corrosion in the studied samples A356.0-type Al-Si-Mg alloy are slightly uniform and predominantly pitting corrosion as obtained by the SEM.

#### 4. CONCLUSIONS

- (1) From the linear polarization and Tafel extrapolation plot, the corrosion rate decreases at all temperatures with the ageing time.
- (2) The corrosion of the DTAT and SQA A356.0-type Al-Si-Mg alloy in the simulated Seawater showed better resistance than the STAT A356.0-type Al-Si-Mg alloy.
- (3) Those samples in the SQA-STAT have improved corrosion resistance than the SQA DTAT samples. The chronopotentiometric corrosion study of some selected samples indicate a decrease and stability in there corrosion resistance with electrochemical exposure time.
- (4) Consequently, the forms of corrosion in the studied A356.0-type Al-Si-Mg alloy are uniform pitting corrosion as obtained from the SEM study with pits diameter ranging from 30-50 $\mu\text{m}$ .

#### ACKNOWLEDGEMENTS

The authors would like to thank the Department of Chemical and Metallurgical Engineering, TUT, South Africa for the equipment support. The technical assistance of Mrs. Adams Feyisayo at Department of Chemistry, University of Johannesburg, Johannesburg, Republic of South Africa during the corrosion test is highly appreciated.

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