Effects of Precipitation Hardening Variables on Al–Zn–Mg-Sn Alloy as Sacrificial Anode in Seawater: Experimental and Statistical Analysis

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Abstract - This research investigated the effects of tin composition and heat treatment variables on the Al-Zn-Mg alloy as sacrificial anode in seawater using gravimetric technique and statistical analysis. Tin was alloyed with Al-Zn-Mg in varied proportions (0%, 0.01%, 0.05% and 0.1%) to determine the optimum anode efficiency in the marine environment. Precipitation heat treatment was performed by first subjecting the samples to solution treatment at 538^{0}C for 2 hours and later subjected to varying hardening temperatures and times. The samples were hardened for 4, 8 and 12 hours at each of the hardening temperatures of 130^0, 160^0 and 190^0 centigrade. The anode efficiency increases as the tin concentration increases. The experimental result of this study showed that the Al-Zn-Mg alloy with 0.1% tin gives the optimum anode efficiency. It was revealed that the Al-Zn-Mg alloy without tin composition exhibited high output current capacity when hardened at 190^{0}C for 4 hours. Predictive model developed in this work was in consonance with experimental observation except the following; at hardening temperature of 160^{0}C, the model recommended 12 hours as against 4 hours of laboratory experiment and at hardening temperature of 130^{0}C it advocated 8 hours as against 12 hours.

Keywords - aluminium alloy, corrosion, precipitation hardening, regression and correlation analysis, and sacrificial anode

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1 INTRODUCTION

Aluminium and its alloys are widely used as sacrificial anode materials in corrosion control for severe environments such as seawater and marine (Yati *et al.*, 2013; Zohdy, 2014; Fagbayi, 2000; Valdez *etr al.*, 2012; El-Hadad *etal.*, 2020; Umoru & Ige, 2007; Ige & Umoru, 2009; Genesca & Juarez, 2007; Zhang, 2014; Ding *et al.*, 2019). The popularity of aluminium as sacrificial anode cathodic protection are due to their cost effectiveness as well as low density, and high current capacity (2980 Ah/kg) (El-Hadad *etal.*, 2020. It has been proved that the efficiency of aluminium anodes is significantly reduced by its ability to form a protective oxide film (Umoru & Ige, 2007; Ige & Umoru, 2009). Thus, there is a need to incorporate elements such as depassivators and modifiers to encourage breakdown of the oxide film and/or shift the operating potential of the metal to a more electronegative direction [3]**.** The most frequently employed depassivating elements are indium (In), mercury (Hg), and tin (Sn). While, gallium (Ga), titanium (Ti) and thallium (Tl) are not often used as depassivators. Some of the commonly employed modifiers include zinc (Zn), magnesium (Mg), barium (Ba), and cadmium (Cd) (Umoru & Ige, 2007; Ige & Umoru, 2009).

In this study, the choice of Al-Zn-Mg system was informed due to its good electrochemical efficiencies (Genesca & Juarez, 2007), feasible metallurgical properties which include the presence of precipitates in α – Al matrix which are capable of breaking down passive films (Zhang, 2014), and being heat treatable metal. Also, addition of tin (depassivator) to the alloy is considered because of its excellent metallurgical properties. The properties include reduced precipitate free zone (PFZ) and the possible interactions of tin with vacancies in the Al matrix, which is expected to change the precipitate morphology in the vicinity of grain boundaries (Zohdy, 2014). Other factors for using tin as depassivator are health, safety, and environmental issues when compared with indium. Lastly, tin is favoured due to its cost effectiveness and encouraging national content being abundantly available in Nigeria. Although, from metallurgical and microstructural studies, there is a good understanding of the performance of Al-Zn-Mg-Sn alloy as sacrificial anode ((Yati *et al.*, 2013; Valdez *et al.*, 2012) but there is no consensus in the mechanism governing the behaviour of Al-Zn-Mg-Sn alloy in terms of anode efficiencies and electrochemical assessments (Yati *et al.*, 2013; Zohdy, 2014; El-Hadad *et al.*, 2020; Umoru & Ige, 2007; Ige & Umoru, 2009; Genesca & Juarez, 2007). A probable explanation may be that corrosion phenomenon are explained from deterministic point of view rather than from probabilistic point of view.

The deterministic approaches to understand corrosion mechanisms are prevalent and of which, electrochemical theory of corrosion is highly favoured. Corrosion is regarded as deterministic quantity because the principles are regarded to be time independent or a random variable. Hence, there are tons of literatures on the atomistic modelling/deterministic approach of corrosion in various environments (Taylor, 2012; Martin, 2004; Kaxtras, 2003; Levine, 2000). Atomistic theory has been widely applied in numerous materials/environment combination and understanding interfacial reactions. However, in reality, the process varies with time and should be characterized as a stochastic process. Hence, corrosion ought to be considered as probabilistic in nature based on the uncertainty principles (Zhang, 2014). While, some researches adopted combination of both deterministic and stochastics theories. There is no consensus on the time when either approaches could be applied. A school of thought believed in the use of deterministic approach during corrosion initiation and completing the corrosion study with probabilistic

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approach at corrosion propagation and growth (Levine, 2000). Another school of thought is of converse viewed that stochastic at the beginning of corrosion and deterministic at the end of the study could be employed (Martin, 2004; Kaxiras, 2003; Levine, 2000).

The above therefore, necessitated this study, in which a statistical investigation to ascertain the optimal tin composition that should be added to Al-Zn-Mg alloy is carried out. Also, the best combination of heat treatment to achieve optimal anode efficiency for the Al-Zn-Mg-Sn alloy is determined in this study.

2 THEORETICAL BACKGROUND

Both deterministic and statistical models have been developed for better understanding of corrosion. Deterministic models are based on fundamental mathematical descriptions and examples of the deterministic types are Euler and Gaussian models (Ige, 2006). On the other hand, statistical models are based on semi-empirical statistical relations among available data and measurements. Statistical models do not necessarily reveal any relation between the cause and the effect. They attempt to determine the underlying relationship between sets of input data (predictors) and targets (predictands) (Zannett, 1990; Hsu, 1992; Bouhamra & Abdul-Wahab, 2004).

Sabah *et al.* (2004) stated that regression analysis can be used to develop a number of predictor models for corrosion based on metal type, location, number of months of exposure, and number of degrading pollutants in the air. The results of their work revealed that additive models showed that copper and mild steel were the most corrosive metals while stainless steel and epoxy were the least corrosive in atmospheric corrosion. Several researchers have stated that most predictive models used are regression models that fit the data such that root mean square error is minimized. They are used to express the relation between the quantity of corrosion and the reasons (Šolić *et al.*, 2019; Sodiki *et al.*, 2016). The predicting equation is obtained by multiple regression analysis.

Generally, multiple regression analysis modelling is effective to identify areas of risk, i.e., correlating among the corrosive factors in an environment and the resultant corrosion and finally obtaining a regression equation for the prediction of the corrosion risk. It is most properly performed on an independent random sample of data. The effect of inputs on the output can be studied using regression coefficients, standard errors of regression coefficients and the level of significance of the regression coefficients. Multiple regression analysis serves three major purposes: (i) description of the relation between variables; (ii) control of predictor variables for a given value of a response variable; and (iii) prediction of a response based on predictor variables (Bouhamra & Abdul-Wahab, 2004; Devore & Peck, 1996; Sen & Srivastava, 1990). It must be noted that during this investigation, all the three purposes will be evaluated. This study involves data collection from experimental set up and they are analysed by statistical method.

The set of data collected may be univariate or multivariate; linear or non-linear; deterministic or stochastic among others (Neter *et al.*, 1996). The datasets can be summarized by data matrices X with n rows and p columns; the rows representing the observations or cases, and the columns the variables. The matrix can be viewed either way, depending on whether the main interest is in the relationships between cases or between the variables. It must be noted that for consistency, the variable of a case by the row vector X. The main division in multivariate methods is between those methods that assume a given structure for example, dividing the cases into groups, and those that seek to discover structure from the evidence of the data matrix alone, it is called data mining nowadays. *Linear models* form the core of classical statistics and are still the basis of much of statistical practice. It is specified by the response vector y and the matrix of explanatory variables or model matrix X. A multiple regression with three quantitative determining variables might be specified as $y \sim X_1 + X_2 + X_3$.

This would correspond to a model with a familiar algebraic specification:

$$y_i = \beta_o + \beta_1 X_{i1} + \beta_2 X_{i2} + \beta_3 X_{i3} + \varepsilon_i, \quad i = 1, 2, \text{----} n \qquad (1)$$

While in linear regression, the mean surface is a plane in sample; in *non-linear* regression model, it may be an arbitrary curved surface but in all other respects, the models are the same. The general form of a non-linear regression model is:

$$y = \eta\,(X_i, \beta) + \varepsilon \qquad (2)$$

Where X is a vector of covariates, β is a p-component vector of unknown parameters and ε is an N (0, σ2) error term (Rao, 1996). Models will be developed for the effect of tin and heat treatment variables on Al-Zn-Mg alloy in seawater in this study.

3 EXPERIMENTAL DETAILS

3.1 MATERIALS

The aluminium alloy used as anode material was obtained from Tower Aluminium Rolling Mills (TARM) situated at an Industrial Estate in Otta, Ogun State, Nigeria. The chemical composition of the alloy was determined using spectrometric technique and it is as listed: 0.166Fe; 0.446Si; 0.003Mn; 0.003Cu; 0.005Zn; 0.019Ti; 0.478Mg; 0.003Pb; 0.001Sn and 98.88Al. The mild steel pipe and welding rod used for setting up the cathodic protection system have their chemical composition analysed as contained in Table 1.

The seawater was obtained from Victoria Island, Lagos and it was subjected to evaporation test which revealed its chloride content as 3.49% by weight.

3.2 CASTING AND HEAT TREATMENT

The aluminium ingot obtained was remelted in a laboratory muffle furnace in the Department of Materials Science and Engineering, OAU, Ile-Ife. The samples were cast in steel die mould into 18 mm diameter rods in order to prepare the required alloy. Four heats of tin treated aluminum were produced with tin content as follows: 0%, 0.01%, 0.05%, and 0.1%. Each of the heats was identified as A, B, C, and D respectively.

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Table 1: Chemical Analysis of the Mild Steel and Welding Rod

Element (%wt)	**C**	**Si**	**Mn**	**S**	**P**	**Cr**	**Ni**	**Sn**	**Cu**	**N**	**Fe**
Mild steel	0.18	0.24	0.45	0.04	0.04	0.10	0.10	0.04	0.25	0.11	98.45
Welding rod	0.15	0.22	0.48	0.04	0.04	-	-	-	-	-	99.07

Table 2: The precipitation hardening temperature and time for the alloys

Sample	A1	A2	A3	B1	B2	B3	C1	C2	C3
Hardening temperature °C)	190	190	190	160	160	160	130	130	130
Hardening time (h)	4	8	`12	4	8	`12	4	8	`12

The 18 mm diameter cylindrical specimens were cut into length of 3.5 mm long, while the mild steel pipes of 30 mm diameter and 55 mm long were also cut. 3 mm diameter holes were drilled in each sample for the purpose of suspension in the media. Thereafter, the samples were soaked at a temperature of 538^{0}C for 2 h. While, oil of 100 SUS was used as quenching medium so as to reduce distortions and cracking associated with water quenching due to high thermal stresses. Artificial precipitation hardening was employed according to Table 2 and subsequently, the samples were air cooled.

3.3 CORROSION MEASUREMENT

The samples surfaces were finished to 600 grits afterwards. All the specimens were washed, degreased in acetone and then dried prior to taking initial weights measurement on a Toledo Mettler balance to 0.001g accuracy. Immediately afterwards, the samples were immersed completely in the seawater. Specimens were removed after every 2 days and weighed after cleaning off the corrosion products. This lasted for 14 days and the seawater environment was maintained at room temperature throughout. Figure 1 shows the connection between the anode and the pipe while the experimental arrangement is as shown in Fig. 2.

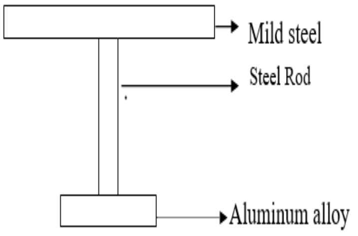

Fig. 1: Sample of the steel rod pipe and Al

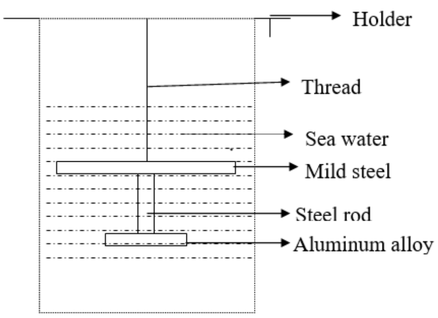

Fig. 2: Experimental arrangement of the corrosion set up rod

The corrosion products formed on the surface of the specimen were removed by scrubbing under running tap water using a fine rubber bung. After swabbing their surfaces with cotton wool soaked in methanol, the specimens were dried and then re-weighed.

3.4 ANODE EFFICIENCY CALCULATION

The anode efficiency (%) was calculated from the following relationship:

$$E(\%) = {CC_A}/{CC_{TH}} \quad X \quad 100 \tag{3}$$

where, CC_A and CC_{TH} are respectively the current capacity of the actual and theoretical anode. The current capacity was calculated using the formula:

$$CC = \frac{It}{(m_i - m_f)} \quad X \quad 100 \tag{4}$$

where I is the current in ampere, t is the time in hours, m_i and m_f are the initial and final weight in grams of the Al anode respectively.

3.5 REGRESSION AND CORRELATION ANALYSIS:

The experimental data observed from the gravimetric technique were analysed based on regression and correlation. Stepwise multiple linear regression analyses were used to develop equations that would best describe the relationship. The evaluations were based on regression and correlation coefficient (r^2) and a level of significance (α) of 0.05 was selected. All statistical analyses were performed with the software package SPSS 7.5.

4 RESULTS AND DISCUSSION

4.1 EFFECT OF TIN ADDITION ON THE AL-ZN-MG ANODE

Figure 3 presents the role of adding tin to the Al-Zn-Mg alloy as sacrificial anode in the studied environment. It was observed that increasing the tin composition resulted in increasing anode efficiency; however, it does not follow a linear relationship with a minimal decrease in the efficiency as the tin content increase from 0.01 to 0.05% having anode efficiency of 98.68 and 98.80%, respectively.

The results showed clearly that the alloy with the maximum concentration of 0.1% Sn demonstrated the optimal efficiency. It can be stated that increasing the tin composition increased the anode efficiency up till 0.1% Sn in the aluminium alloy (Ige & Umoru, 2007). It has been reported that increasing the tin composition leads to grain refinement and better cathodic performance (Ding *et al.*, 2019). Aluminium anode efficiencies according to National Association of Corrosion Engineers (NACE) and Det Norske Veritas (DNV) standards should have current

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capacity between 2300 and 2700 A-hr/Kg (Suarez *et al.*, 1999). In this study, the calculated Faradaic efficiencies of the aluminium anode alloys containing 0%, 0.01%, 0.05% and 0.1% tin are respectively 2713 A-hr/Kg, 2775 A-hr/Kg, 2684 A-hr/Kg and 2589 A-hr/Kg. thus, it can be inferred that only anodes with 0.05% Sn and 0.1% Sn have their current output capacity in this range.

4.2 EFFECT OF PRECIPITATION HARDENING VARIABLES (TEMPERATURE AND TIME) ON THE AL-ZN-MG ANODE

It was noticed that alloying the Al-Zn-Mg with tin at precipitation hardening temperature of 190°C irrespective of the hardening time does not have beneficial effects on the anode efficiency of the sacrificial anode (Figure 4a**)**. In fact, alloying with 0.05% Sn have the worst performance, most especially at 8 h. Interpreting both Figures 4a and b concurrently, it can be ascertained that at 160 and 190°C, there is no clear trend but samples without tin have poor performance. The role of hardening time revealed that there is a linear relationship at 4 and 12 h while the relationship is parabolic at 8 h.

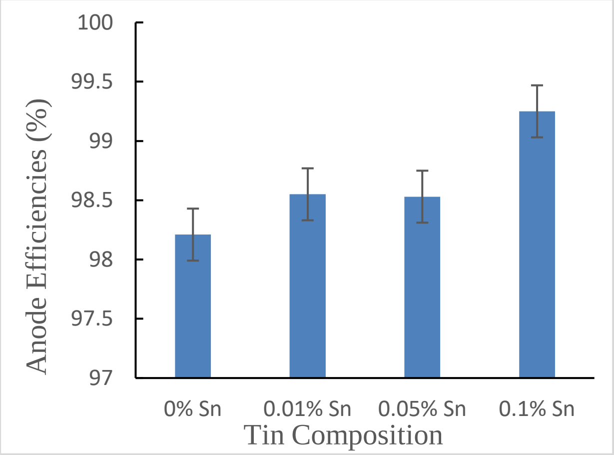


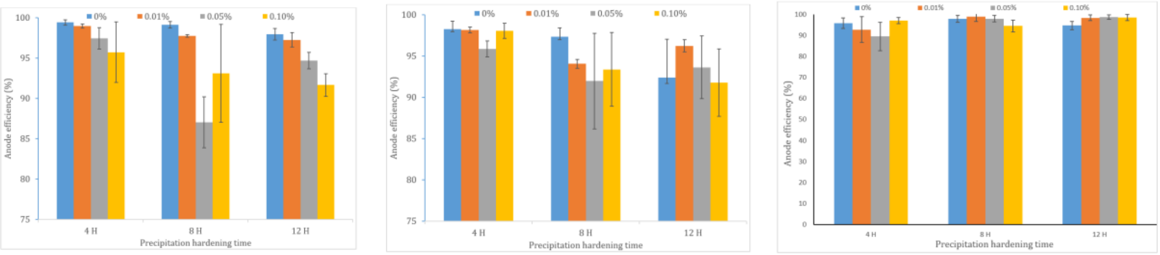
Fig. 3: Anode efficiency showing effect of tin on the Al-Zn-Mg alloy

A noticeable pattern was that the anode efficiencies of the alloy were higher at lower ageing periods (4 h and 8 h) with alloy that was aged for 4 hours exhibited the highest cathodic protection. Similar trend was observed for samples hardened at 160°C. The anode efficiency was optimum for sample without tin. The exceptions are samples subjected to 12 h where the sample with 0.01% have the optimum efficiency. There is no clear pattern in their behaviour (Ige, 2006). A possible explanation is that the depassivation process is attributed to the formation of particulate precipitates and the reinforcement of Zn along the aluminium alloy matrix. These precipitates assist in the breakdown of the film. As a result of the higher energy field around the grain boundaries, they are the preferred sites for the segregation of the precipitates. The resultant dislocation pile- ups at grain boundaries and the consequent high local stresses are assumed to be assisting in the preferential fracture at the boundaries and causing break down of the network of passivating film. It is suspected that the precipitates (incoherent) appeared in the early hours of the heat treatment and disappeared later probably due to diffusion of the precipitates and homogenization of the matrix. The increased anode efficiency of the alloy precipitation hardened at 190°C for 4 hours suggests that this has been possible because of the ability of the precipitates to depassivate the surface of the aluminium alloy anode.

The results for samples hardened at 130°C (Figure 4c) revealed that increasing the tin content and hardening time improve the anode efficiency. This can be attributed to the same factor that accounts for hardening at 190°C which is due to the reason that at this hardening time the precipitates are still at transitional phases. These transitional phases give better resistance to corrosion than equilibrium θ phase. Since diffusion/precipitation processes are slower at lower temperatures than higher temperatures, the precipitates appeared in the aluminium matrix only after aging for longer periods (Abdul-Wahab *et al.* 2004; Sen & Srivastava, 1990). Meanwhile, at 12 H, the anode efficiency increased linearly at lower hardening temperature of 130°C with sample having 0.1% Sn having optimum efficiency. Thus, it can be recommended that at lower temperature regimes, the Al-Zn-Mg-Sn anode should be treated at longer aging period to produce higher efficiencies (Ige & Umoru, 2009**)**.

4.3 REGRESSION AND CORRELATION ANALYSIS

Statistical analysis based on regression and correlation was adopted to examine the role of tin on the compositional analysis of the Al-Zn-Mg system on one hand and the effect of precipitation hardening variables on the other hand. The outcome of the analysis was presented in Table 3 (Ige, 2006**)**. Model development was achieved using coefficient of determination (r^2), the level of significance is 0.05, and the obtained data are highly correlated. The least value of the correlation coefficient is obtained when the samples are precipitation hardened at 160 °C for 8 h ($r^2 = 0.729$). While the maximum value is obtained when the samples are precipitated hardened at 190 °C for 8 h ($r^2 = 0.976$). The samples that are not heat treated gives correlation coefficient of 0.96. The least value obtained for samples that are precipitated hardened at 190 °C is 0.877 and it occurs at hardened time of 4 h and the highest occurs at 8 h (0.976).



(a) (b) (c)

Fig. 4: The effect of precipitation hardening time on the anode efficiency of Al-Zn-Mg after aging at (a) 190 °C (b) 160 °C (c) 130 °C

Meanwhile, the maximum value and the least value for samples at 160°C are obtained at hardening time of 12 h and 8 h respectively (i.e., $r^2 = 0.966$ and $r^2 = 0.729$). The least correlation for 130°C is obtained at 4 h ($r^2 = 0.756$) and the maximum at 12 h ($r^2 = 0.910$) (Ige, 2006).

The simple multiple regression analysis for estimation of the anode performance of the Al-Zn-Mg-Sn alloy for the seawater environment can be expressed as:

$$Y = a - b_1X_1 + b_2X_2 - - - - - - - - - - - - - - + b_nX_n \qquad (5)$$

Where, Y is the anode performance, A is the constant

b_1, b_2 - - - b_n are the coefficients

X_1, X_2 --- X_n are the variables (i.e., tin compositions).

The models were developed based on the regressor matrix of covariance and the model equations are as presented in Table 4. It is observed that the models depict linear relationship among the variables and they can be solved mathematically by using matrices method. The solutions obtained at the first iteration are as follows:

0.1% Sn = 40.86 (23.87%); 0.01% Sn = 10.61 (6.20%); 0.05% Sn = 28.24 (16.50%) and 0.1% Sn = 91.46 (53.43%).

There are significant correlations ($p < 0.05$) for the factors under investigation [(Ige, 2006). The regression models for the various tin compositions established that there is a statistically significant relationship among the factors. Generally, a multiple correlation coefficient of 0.5 or above is considered a high relationship and when the correlation coefficient (r^2) is 1, it indicates a perfect correlation exists and when it is 0, it implies that the equation is not helpful (Sen *et al.*, 2002). It is observed that the results are highly correlated ranging from 0.729 to 0.976 with the least values associated with samples treated at 130°C and the most correlated at 190 °C respectively. Surprisingly, it is observed that the least coefficient of determination for samples that are hardened at 190°C is obtained at hardened time of 4 h ($r^2 = 0.877$) and the highest at 8 h (0.976). While at hardening temperature of 160°C the least correlation is obtained at 8 h and the highest at 12 h whereas for samples treated at 130°C the correlation coefficient increases as the hardening time increases.

The physical description of the model is based on the additive or subtractive effects of the individual tin composition of the alloys. It is discovered that for samples without heat treatment, the alloy composition effects are subtractive with the least effect observed with sample of 0.1% Sn. This implied that the alloys with the least coefficient will contribute positively to the performance of the anode. Additive effects were observed for samples subjected to various precipitation hardening temperatures. Sabah et al., (2004) observed that the additive effect will reinforce and improve the performance of regression model and as such confers good performance on them. The alloy with the least coefficient is the one with 0.1% Sn and this is in consonance with the experimental result but the model predict that the most negative effect is attributed to 0.01% Sn as against 0% Sn obtained from the laboratory work. It is revealed that the samples that are treated at 190°C for 4 h give the highest constant and as such tends to be the highest value obtainable and it is noted that the additive effect is on the sample with 0.1% Sn as against the best efficiency obtained from sample without tin.

Table 3. Model Summary for the Regression and Correlation Analysis

S/N	Types of Treatment	R	R²	Adjusted R²	F	Std Error of Estimate
1	AR	0.983	0.966	0.899	14.42	32.88
2	A1	0.937	0.877	0.632	3.75	62.92
3	A2	0.988	0.976	0.929	20.52	27.70
4	A3	0.949	0.902	0.705	4.58	56.36
5	B1	0.976	0.952	0.856	9.95	39.28
6	B2	0.854	0.729	0.188	1.35	93.46
7	B3	0.983	0.966	0.899	14.42	32.88
8	C1	0.869	0.756	0.268	1.55	88.72
9	C2	0.942	0.887	0.660	3.91	60.50
10	C3	0.954	0.910	0.730	5.05	53.90

Table 4: Multiple Linear Regression Equations of the Tin Compositions in the Alloy

S/N	Types of Treatment	Model
1	AR	1530 – 3.95A – 5.85B – 5.14C – 0.59D
2	A1	3560 – 12.1A – 27.9B – 38.6C + 0.33D
3	A2	1050 – 13.4A + 2.7B + 23.3C – 11.48D
4	A3	1050 – 25.7A + 11.1B + 4.70C – 0.71D
5	B1	593 - 1.32A – 2.41B – 21.0C – 4.74D
6	B2	734 – 8.93A – 69.2B – 1.34C + 3.49D
7	B3	963 – 0.9A – 11.7B + 5.4C – 14.4D
8	C1	1350 – 4.95A + 5.69B – 0.08C – 14.4D
9	C2	1128 + 5.5A + 2.5B + 20C + 0.35D
10	C3	1330 + 0.29A + 1.42B – 10.9C – 4.28D

The most efficient of the samples treated at 160°C are the ones hardened at 12 h and this is attributed to the positive contribution of the additive effects. It is noted that the samples treated at 130°C for 8 h give the best performance than any other model. Average performances were obtained for samples hardened for 12 h at different temperatures, with the most efficient being the samples treated at 130°C (Ige, 2006).

The mathematical solution obtained from the models by matrices method indicates that the best performance of the Al-Zn-Mg-Sn alloy will be obtained from composition with high percentage of 0.1% tin, followed by 0.05% Sn while the least will be 0.01% Sn [14]. The experimental data were in agreement with the model predictions in that the anode efficiency increases with the tin composition and optimum variables are the ones at 190°C for 4 h. Also, the samples that are treated at 12 h for different temperatures are in agreement for both laboratory and model predictions with samples hardened at 130^{o}C having the best performance. However, the best variables at hardening temperature of 160°C is obtained at hardening time of 12 h while the model predicts that the worst performance will be obtained from samples treated at 4 h. This is in contrast with the values obtained from the laboratory. Similar trend was observed for samples treated at 130°C where the models predict that the best performance will be obtained at 8 hours and the experimental work advocates 12 h.

The model predicts for the samples that are hardened at 8 h for different hardened temperatures to have the best performance at 130°C while experimental data indicates 190°C. This may be attributed to the pronounced additive effects observed from the model of samples hardened at 130^{o}C for 8 h.

5 CONCLUSION

On the strength of the results obtained in this work, the following conclusions can be drawn:

- The model prediction agreed with the experimental data in respect of optimum determination of the tin that can be alloyed with Al-Zn-Mg
- At hardening temperature of 130°C, the model forecast that the most efficient performance is at 8 h while the experimental data indicates 12 h.
- The model predicts that the best performance will be obtained at hardening time of 12 h for hardening temperature of 160°C as against the laboratory data of 4 h.
- When the hardening time is 8 h the experimental data advocates hardening temperature of 190°C as against 130°C of the model.
- The use of other forecasting or probabilistic techniques such as neural network and time series analysis is strongly advocated for the model analysis and development.

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