Development of 93.95Al-5Zn-1.05Sn Ternary Alloy and Its Response to Ageing

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***Abstract*—This work has outlined the development of a hard- light ternary alloy (93.95Al-5Zn-1.05Sn), the alloy was produced in the foundry shop of the National Metallurgical Development Centre, Jos. After the production of the alloy, hardness test specimens were prepared in accordance with JIS standard for Hardness test. Rockwell hardness tester was used with the scale adjusted to scale B, before the commencement of the tests the machine was checked for calibration using a standard test block. Ageing was conducted on all the test specimens except the control specimen before the hardness measurements were taken as described above. The results generated were then analyzed statistically to ascertain the degree of response of the ternary alloy to age hardening. The alloy had a hardness value of 32.33HRB in the as- cast condition. On age hardening the hardness gradually dropped within the four hours ageing period. Interestingly, the peak nature of all age hardening alloys was manifested in the ternary alloy at two hours of ageing corresponding to a hardness value of 27.13 HRB; a good indication that the ternary alloy responded to age hardening treatment. The Product Moment Coefficient of Correlation (r) between hardness and ageing time was 0.26, this confirmed 26% linear relationship, and the balance was more of a nonlinear nature since the data exhibited conspicuous response to age hardening. Significance test was conducted on r which confirmed that the relationship between the hardness and the ageing time was nonlinear. The analysis further looked at a predictive model; its level of significance, standard error of regression, and the confidence limits of the results generated from the predictive model.**

Keywords—Response, Age hardening, Time, Ternary alloy, Development, Statistics

1. INTRODUCTION

The basic structural changes or morphological changes on age hardening are brought together by the different stages of disintegration of the saturated solid solution resulting from hardening of the alloy. Since disintegration of the saturated solution is a diffusion controlled process, the degree of disintegration, type of precipitation from the solution, their dispersion, form, and other structural characteristics depends on the nature of the alloy and its chemical composition. Besides the structure of an age-hardened material, it also depends on impurities, heating temperature, velocity of cooling, on hardening, plastic deformation after hardening, duration of weathering of the hardened alloy at room temperature before artificial hardening and many other factors. The effect of all these factors combined makes a study of the process of age hardened alloy and composites difficult [1-5]. Age hardening assists in the distribution of the particles in the matrix and this goes a long way to improve the mechanical properties. In age hardening no phase transformation takes place what happens is precipitation [1-5]. This increases hardness of the material.

The greatest strength in any known aluminium alloy is obtained by the addition of zinc and magnesium (e.g. 8 wt. percent Zn, 1 wt percent Mg), which form zones and intermediate precipitates leading towards the stable $MgZn_2$ compound. The binary Al-Zn system has favourable solubility and zone and intermediate precipitate characteristics but is not a good age hardening system, at room temperature, because the zinc atom is too mobile and the coarse equilibrium precipitate (Zn) forms at quite low temperature by continuous and discontinuous precipitation [5-6]. Many commercial alloys are greatly improved by the addition of various elements in trace amounts, which are able to enhance or retard the formation of various structures. For example, Cu-Be alloys soften rapidly by discontinuous precipitation at temperatures above about 300°C, but this can be prevented by the addition of about 0.4 wt. percent cobalt. This trace element retards the formation of G.P. Zones and so delays the age hardening process at room temperature, which gives more time for mechanically fabricating the quenched alloy before it becomes too hard (otherwise the quenched alloy has to be refrigerated to keep it soft); and it speeds up the formation of Θ' and also leads to a greater hardness from this precipitate. This work has used 1.05 wt. percent tin as the trace element in the Al-Zn alloy system. Much effort has gone into the study of trace elements in Al-Zn-Mg alloy [3,5]. Although very hard, the basic alloy is plagued by grain boundary weakness due to precipitate-free regions. Small additions of silver have a very beneficial effect in refining the precipitate structure and removing the precipitate-free regions. According to Khanna [3] low tin aluminium alloys possess high fatigue strength and thus can carry fluctuating loads. Literature review has shown that 93.95Al-5Zn-1.05Sn alloy is not a common alloy, therefore the effect of 1.05 wt. percent tin on Al-Zn alloy system will be interesting to investigate particularly as it response to ageing. Mg is commonly used but in this work it is replaced by tin.

Alloying is used in many different ways to strength metals. The most important general method is to obstruct the movement of dislocations by a fine dispersion of foreign particles distributed throughout the matrix crystal. Alloys sometimes form solid solutions which obey Hume Rothery's [3] rules but in many binary alloy systems, when the chemical affinity of metals is great, their mutual solubility becomes limited and intermediate phases are formed rather than solid solutions. Intermediate phases are the phases that form in the intermediate composition regions of the equilibrium diagram. They are separated from the pure metals or other adjacent phases on the equilibrium diagram by two phase fields of immiscibility, and which have crystal structure different from those of pure components of which they are composed. Intermediate phases may be classed as two types: a) intermetallic compounds of fixed composition b) intermetallic compounds of variable composition [3].

The objective of this research work is to develop a ternary alloy with Mg replaced with Sn in the familiar Al-Zn-Mg system and to also investigate the response of the ternary alloy to age hardening treatment.

2 MATERIALS AND METHOD

2.1 Materials

The materials used for the work included; aluminium cables from Cocanaco Cable Company from Kaduna, pure zinc and tin from National Metallurgical Development Centre, Jos stock.

The equipment used included cutting saw, weighing balance, mechanical stirrer, oven, Rockwell hardness tester, grinding and polishing machine, ball mill, nest of sieves and sieve shaker, permanent metal moulds and melting furnace.

2.2 Method

The production of the ternary alloy (93.95Al-5Zn-1.05Sn) was carried out in the foundry shop of the National Metallurgical Development Centre (NMDC) Jos, where 93.95% Al, 5%Zn, and 1.05%Sn were melted in the furnace and poured into permanent metal moulds.

The specimens were removed and prepared into test pieces for hardness test using Rockwell tester. The specimens were prepared in accordance with JIS standard for preparing specimens for hardness test [7]. They were then subjected to age hardening heat treatment. The treatment involved solutioning at 500^{O}C, quenching in warm water, drying with air blower, ageing at a constant temperature (150^{O}C) and varying the ageing time from 1hr to 4hrs. The details of the hardness test were: Rockwell Hardness 'B' Scale was used, the minor load was 98N (9.8Kgf), the major load was 980N (100Kgf), the indenter was hardened steel ball (1.8mm), the standard test block hardness value was 101.2HRB and the test temperature which was the room temperature was 27^{O}C. The machine was checked for calibration using standard test block before the commencement of the hardness test. The result of the test is as presented in Table 1. This work was done in NMDC foundry as earlier stated. All other variables were kept constant; ageing time was the only independent variable.

3. RESULTS AND ANALYSIS

3.1 Results

Table 1 show hardness values of the ternary alloy at different age hardening times

Table 1 Hardness Values of 93.95Al-5Zn-1.05Sn Ternary Alloy at Different Ageing Times

S/No	Ageing Time (hrs)	Solution Temp. (^{o}C)	Ageing Temp. (^{o}C)	Hardness (HRB)
1	0	As Cast	As Cast	32.33
2	1	500	150	26.00
3	2	500	150	27.13
4	3	500	150	27.00
5	4	500	150	26.40

3.2 Analysis

Using the result in Table 1 above the product moment coefficient of correlation (r) can be calculated as below:

Product Moment Coefficient of Correlation (r)

This coefficient gives an indication of the strength of the linear relationship between two variables

$$r = \frac{n\sum xy - \sum x \sum y}{\sqrt{n\sum x^2 - (\sum x)^2} \; X \sqrt{n\sum y^2 - (\sum y)^2}} \quad (1)$$

Table 2 Determination of r

N	x(Ageing Time)	Y (Hardness, HRB)	x^2	y^2	xy
1	1	26.00	1	676.00	26.00
2	2	27.13	4	736.04	54.26
3	3	27.00	9	729.00	81.00
4	4	26.40	16	696.96	105.60
	10 Σx	106.53 Σy	30 Σx^2	2838 Σy^2	266.86 Σxy

Inserting the values in Table 2 in equation 1

Product moment coefficient of correlation (r) = 0.26

The correlation coefficient is 0.26 which indicates a low positive linear association between ageing time and hardness of the ternary alloy. The linear relationship is very weak between the two variables. There may be a strong relationship between these variables but of a nonlinear kind [11].

The Significance of r

Ho: ρ = 0

H1: ρ ≠ 0

$$|t| = \left|\frac{r-\rho}{\sqrt{1-r^2}} \times \sqrt{n-2}\right| \quad (2)$$

Substituting r= 0.26 and n = 4 into equation 2 we have

|t| = 0.38

The tabulated value for n-2 for 2 degrees of freedom using a 5% level of significance is 5.991, since 0.38 the calculated value is less than 5.991 the numerical evidence is strong enough to accept the null hypothesis and conclude that the value of ρ is zero. The significance test still confirms the product moment coefficient of correlation, which means the existing relationship is more of nonlinear. The product moment coefficient of correlation actually indicates that the linear relationship is just 26% and the nonlinear which is the balance is 74% [12].

Calculating the Values of a and b

The basic two variable models (one dependent and one independent variable) is

$$Y = a + bx \quad (3)$$

Where a and b are constants and a represent the fixed elements and b the slope.

Which can be solved using the normal equations thus:

$$\sum y = an + b\sum x \quad (4)$$

$$\sum xy = a\sum x + b\sum x^2 \quad (5)$$

Where,

n, is number of pairs of figures, a and b are constants representing the intercept and the slope. b is called the regression coefficient, x and y are the variables representing the independent and dependent variables.

From equations 4 and 5 and Table 2 the values of a and b are

$a = 26.37$

$b = 0.107$

The regression line is therefore

$$y = 26.37 + 0.107x \quad (6)$$

Accuracy of Regression Line

Coefficient of Determination (r^2)

$$r^2 = \frac{Explained\ Variation}{Total\ Variation} = \frac{\sum(YE-\mathcal{Y})^2}{\sum(Y-\mathcal{Y})^2} \quad (7)$$

Where

YE = Estimate of y given by the regression equation for each value of x

$\mathcal{Y} = mean\ of\ actual\ values\ of\ y$

Y = Individual actual values of y

$r^2\ for\ y = 26.37 + 0.107x$

$\mathcal{Y} = \frac{106.53}{4} = 26.63$

Table 3 Calculation of Coefficient of Determination

X	Y	YE	YE-$\mathcal{Y}$	(YE-$\mathcal{Y}$)^2	Y-$\mathcal{Y}$	(Y-$\mathcal{Y}$)^2
1	26.00	26.48	-0.15	0.0225	-0.63	0.3969
2	27.13	26.59	-0.04	0.0016	0.5	0.25
3	27.00	26.70	0.07	0.0049	0.37	0.1369
4	26.40	26.81	0.18	0.0324	-0.23	0.0529
	106.53			0.0614		0.8367

$r^2 = \frac{0.0614}{0.8367} = 0.073$

$100r^2 = 7.3\%$

This result may be interpreted that in the hardening of the alloy during age hardening; 7.3% of the variation in hardness may be predicted by change in the actual value of x which is the ageing time of the alloy at the ageing temperature. Factors other than ageing time (x) account for 92.7% of the variation in the hardness y of the ternary alloy. The accuracy of the regression line model is therefore very low and cannot be relied upon for predictive purposes. Another implication of the low value of r^2 is that the relationship between ageing time and hardness values of the alloy may be a non-linear relationship which is the most probable thing based on previous works [8-11]. A nonlinear predictive model will therefore offer a high accuracy than the linear model.

Standard Error of Regression

Standard error of regression=

$$Se = \sqrt{\frac{\sum y^2 - a\sum y - b\sum xy}{n-2}} \quad (8)$$

From equation 8

Standard error of regression (residual standard deviation) = 0.1

Setting Confidence Limits

The confidence limits for the whole of the regression line are calculated by using a quantity known as the standard error of the average forecast which is given by

$$S_{ef} = Se\sqrt{\frac{1}{n} + \frac{(x-\mathcal{X})^2}{\sum x^2 - \frac{(\sum x)^2}{n}}} \quad (9)$$

$\sqrt{\frac{1}{n} + \frac{(x-\mathcal{X})^2}{\sum x^2 - \frac{(\sum x)^2}{n}}}$ varies according to the value of x.

1/n and $\sum x^2 - \frac{(\sum x)^2}{n}$ are a constant for a particular problem $(x-\mathcal{X})^2$ must be calculated for each value of x.

1/n = ¼ =0.25 $\sum x^2 - \frac{(\sum x)^2}{n} = 30 - \frac{10^2}{4} = 30 - 25 =$ 5 $\bar{x} = \frac{10}{4} = 2.5$

The expression $(x - \bar{x})^2$ will vary as follows:

X=1 $(1\text{-}2.5)^2$ 2.25

X=2 $(2\text{-}2.5)^2$ 0.25

X=3 $(3\text{-}2.5)^2$ 0.25

X=4 $(4\text{-} 2.5)^2$ 2.25

The expression $\sqrt{\frac{1}{n} + \frac{(x-\bar{x})^2}{\sum x^2 - \frac{(\sum x)^2}{n}}}$ may now be evaluated

When

X= 1 $\sqrt{\frac{1}{n} + \frac{(x-\bar{x})^2}{\sum x^2 - \frac{(\sum x)^2}{n}}}$ = 0.84

X= 2 $\sqrt{\frac{1}{n} + \frac{(x-\bar{x})^2}{\sum x^2 - \frac{(\sum x)^2}{n}}}$ = 0.55

X= 3 $\sqrt{\frac{1}{n} + \frac{(x-\bar{x})^2}{\sum x^2 - \frac{(\sum x)^2}{n}}}$ = 0.55

X= 4 $\sqrt{\frac{1}{n} + \frac{(x-\bar{x})^2}{\sum x^2 - \frac{(\sum x)^2}{n}}}$ = 0.84

Constructing the Confidence Interval

a=26.365, b=0.11, Se=0.1, degree of freedom =2

S_{ef} = Se $\sqrt{\frac{1}{n} + \frac{(x-\bar{x})^2}{\sum x^2 - \frac{(\sum x)^2}{n}}}$ = 0.1 x value from calculations above, and t = 4.303 for 2 degrees of freedom and a 95% confidence interval.

The confidence interval can now be calculated as follows:

When x= 1, y= 26.37 + 0.11 x1 =26.48

The limits round this estimate are $26.48 \pm 0.1x0.84x4.303 = 26.48 \pm 0.36$ this gives an upper limit of 26.84 and a lower limit of 26.12

X =2 y = 26.59 26.59 ± 0.24

X= 3 y = 26.70 26.59 ± 0.24

X = 4 y = 26.81 26.59 ± 0.36

Table 4 Calculated Confidence Interval

X	Y	Confidence Interval: Lower limit	Confidence Interval: Upper limit
1	26.48	26.12	26.84
2	26.59	26.35	26.83
3	26.70	26.46	26.70
4	26.81	26.45	27.17

Confidence interval for Individual Predictions

Standard error of the individual forecast is shown below

S_{ef} (individual) = Se $\sqrt{1 + \frac{1}{n} + \frac{(x-\bar{x})^2}{\sum x^2 - \frac{(\sum x)^2}{n}}}$ (10)

For x = 2

S_{ef} (individual) = 0.11

When x = 2, y = 26.59 which have individual confidence interval of 26.59 ± 0.49 giving a lower limit of 26.1 and a upper limit of 27.08. when contrasted with the general confidence interval above, which when x was 2 the range was 26.35 to 26.83 it can be seen that when an individual prediction of y is made, the confidence intervals are much wider.

Standard Errors of the Intercept (a) and Gradient (b)

The intercept Sa = $\boldsymbol{Se}\sqrt{\frac{\sum x^2}{n\sum x^2 - (\sum x)^2}}$ (11)

The gradient $S_b = \frac{Se}{\sqrt{\sum x^2 - \frac{(\sum x)^2}{n}}}$ (12)

Where S_e is the standard error of regression, the confidence interval for $\propto$ *and* β may be established as follows:

For the intercept

$\propto = a \pm t\ x\ Sa$ (13)

For the gradient

$\beta = b \pm t\ x\ Sb$ (14)

Test of Significance for $\propto$ *and* β

For Intercept

Ho: $\propto = some\ chosen\ value$

H_1: $\propto \neq some\ chosen\ value$

The test statistics is

$t = \frac{a - \propto}{Sa}$ (15)

For the Gradient

H_O: $\beta = 0$

H_1: $\beta \neq 0$

The test statistics is

$t = \frac{b - \beta}{S_b}$ (16)

Applying these values, n =4, a= 26.37, b= 0.11, t = 4.303, Se = 0.1, $\sum x^2 = 30, \sum x = 10$ into equation 11

The standard error of the intercept $(S_a) = 0.12$

The 95% confidence interval of the intercept is $\propto = 26.37 \pm 0.53$

Which gives an upper limit of 26.9 and a lower limit of 25.84.

Significance test for the intercept

H_o: $\propto = 0$

H_1: $\propto \neq 0$

Applying test statistics in equation 15

$t = 219.75$

Since 219.75 is much greater than 4.303 (the value from t table), Ho can be rejected.

Standard error of the slope (S_b) from equation 12 = 0.045

The 95% confidence interval for the slope is $\beta = 0.11 \pm 0.19$ giving an upper limit of 0.3 and a lower limit of -0.08

Significance test for slope

H_O: $\beta = 0$

H_1: $\beta \neq 0$

The test statistics in equation 16 now gives $t = 2.44$

Since 2.44 is less than 4.303, H_o can be accepted on the basis of this evidence the regression equation

$y = 26.37 + 0.11x$

Cannot be used as a basis of prediction for the hardness of age hardening ternary alloy, it can only be used as a crude estimate for determining the response of age hardening in the ternary alloy.

The analysis has shown that there is a relationship between ageing time and hardness values of the ternary alloy. This can also be seen in Table 1, however the relationship is a nonlinear relationship which makes the accuracy of the regression line to be very low (7.3%). The drop in hardness value of the ternary alloy from the as cast value of 32.33 HRB can be explained; it is caused by the solution treatment given to the alloy, normally when nonferrous alloys are quenched they become soft, it is the age hardening treatment that increases the alloy hardness again [4]. This analysis agrees with previous works conducted by several researchers [8-12].

4 Conclusions

The study 'Development of 93.95Al-5Zn-1.05Sn Ternary Alloy and its Response to Ageing' has been extensively investigated using the generated result from the test conducted on the ternary alloy and statistical analysis. The following conclusions are hereby drawn:

1. the developed ternary alloy responded to age hardening treatment,
2. the statistical analysis showed that there is a low linear relationship between the ageing time and the hardening of the alloy as indicated by a product moment coefficient r of 0.26,
3. the work developed a predictive model which was tested and only had an accuracy of 7.3%, and based on the standard error and confidence limits of the regression line model the predictive model can be used only as a crude means of estimation, and
4. finally the main objectives of the work has been achieved with the development of the alloy and establishing that it can respond to age hardening.

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