Model for predicting and analyzing the %Fe removed as deleterious element from Al-Si alloys during Fe removal processing with Mn

F. A. Anene and N. E. Nwankwo*

Metallurgical and Materials Engineering Department, Nnamdi Azikiwe University, Awka, Nigeria

*Correspondence Info:
N. E. Nwankwo
Metallurgical and Materials Engineering Department,
Nnamdi Azikiwe University, Awka, Nigeria
E-mail: nkemnwankwo60@yahoo.com

Abstract

Model equation for predicting and analysing %Fe removed from a eutectic Al-Si alloy during Fe removal processing with Mn under controlled conditions has been derived and validated. The model derived; % Fe removed = +1.30700 + 0.095882* Al-Si + %Mn - 0.068512* Al-Si + %Mn^2 + 9.77000E-003* Al-Si^+*Mn^3, is found to predict the %Fe removed from Al-Si alloy as a cubic function of Mn content, With a standard deviation of 0.010. Analysed results obtained show that %Fe removal equation with Mn addition has been validly derived. The model "R-Squared" of 0.9814 is found to be in agreement with the "Adj R-Squared" of 0.9628; the difference being less than 0.2. The derived model equation gives a reasonable forecast of %Fe removed very close to the values obtained from the experiments. The close proximity of both model and experimental result values is attributed to the low standard error of the model coefficients. The processing parameters are process temperature, alloy contents and holding time.

Keywords: Model, Predicting, %Fe removed, Deleterious element, Al-Si alloy.

1. Introduction

Al-Si alloy has been an important commercial cast Al alloy most commonly used because of its high strength, castability and good corrosion resistance. The alloys are applied widely in foundry for ingots and component castings mainly of automobile parts. Specific Al-SiCo alloy has been developed with high strength and high resistivity which is useful in high resistivity electrical motor [2]. The scope for its utilization continues to widen because of its light weight advantage which gives it a higher strength to weight ratio when compared with other cast alloys and materials.

The low mechanical and technological properties of the secondary Al materials are caused by the high content of other elements especially deleterious Fe impurities [1]. Fe and Fe-containing compounds in excess of the Fe critical level act as strain raiser and point of weak coherence which reduce the mechanical properties through stress induced micro cracking and casting defects such as oxide formation and porosity in mouldings that hinder the use of the alloys in foundry productions of cast components [2]. The initiation of micro cracks can be influenced by the presence and nature of second phase particles. A common situation is for the particles to crack during deformation. Resistance to cracking improves if the particle is well bonded to the matrix. Small particles (r less than 1μm) and spherical particles are more resistant to cracking [10]. Fe may slightly increase the strength of an alloy, but drastically decreases the ductility, especially if above 0.7% Fe and not corrected by Mo, Cr, etc. Fe is found to be even more deleterious when it combines with other elements present to form insoluble complex intermetallic precipitates. Binary Al-Si alloys and other cast Al alloys can be polluted by Fe in several ways; through contaminated Al oxide ore, use of metal mould or by the processing equipment and tools. Over the years and in the world today, various substances such as heavy metals have polluted our environment. Contamination by heavy metals in air, soil and water has severe effects on level of biological organism (that is, from cell to ecological systems) and are global problems that are threats to humanity [3].

The use of Mn, Co, Ni, Mo and other elements as Fe-removing elements have been investigated and severally reported by many authors and more recently confirmed in the study of metallurgical techniques for improving the physical and mechanical properties of Al-Si alloys and its effects found to vary with dopant contents [2]. Varied contents of dopants resulted in various %Fe removed from Al-Si alloys and changes in mechanical properties depending on what phase (β- AlSiFe or α- AlSiFe) is formed [4]. The result of the mechanical
properties can be explained on the basis of the quantity of Fe removed which was confirm by the high percentage of Fe removal fraction recorded in the investigation of Nwankwo et al.[12]. The mechanism of Fe removal by metallic dopants based on sludge formation has also been previously reported. The sequence for the mechanism of Fe removal from Al-Si alloy is the formation of primary Fe-rich intermetallic compound, entry into sludge and subsequent removal from the melt by filtration or other methods [5].

Thus Fe removal from Al-Si alloys with transitional metals is achievable to satisfactory levels and the main parameters known to affect the iron removal process include metal addition, holding time and processing temperature [6].

Previous Studies on Fe removal experiments report that the crystal structure of the precipitate Al₁₅(FeMn)₃Si₂ depends on the Mn/Fe ratio and the Fe content generally decreases from 1-2 wt % to at most 0.4 wt % after treatment with applicable metals [7]. It was found that the most effective Mn/Fe ratio for Fe removal from Al-Si alloys is to be 2/1 [8 and 2] thereby removing Fe content by 87% and 74% respectively. This is further confirmed by several micrographs of the Fe-corrupted alloys which reveal detail microstructural morphologies of cast Al-Si alloys [5].

Nwoye et al[9] derived a model for calculating the concentration of leached iron during leaching of iron oxide ore in sulphuric acid solution. The model is expressed as; %Fe = e-2.0421(InT) . The model was found to predict %Fe (leached) very close to the values obtained from the experiment, being dependent on the values of the final leaching solution temperature measured during the leaching process. It was observed that the validity of the model is rooted in the expression ln(%Fe) = N(InT) where both sides of the expression are correspondingly approximately equal. The positive or negative deviation of each of the model-predicted values of %Fe (leached) from those of the experimental values was found to be less than 37%, which is quite within the range of acceptable deviation limit for experimental result.

Nwoye et al[11] also formulated a model for predicting the concentration of phosphorus removed during leaching of iron oxide ore in oxalic acid solution. The model is expressed as; \( P = 150.5/\mu \).

It was found to predict the removed phosphorus concentration, with utmost dependence on the final pH of the leaching solution and weight input of the iron oxide ore. The model indicates that the concentration of phosphorus removed is inversely proportional to the product of the weight input of the iron oxide ore and the final pH of the leaching solution. Process conditions considered during the formulation of the model include: leaching temperature of 250°C, initial solution pH 5.5 and average ore grain size; 150μm).

The present study is aimed to derive model equation to further assist scientific efforts in predicting and computational analysis of %Fe removed from Al-Si alloys designated for special applications using given levels of Mn additions. The derived model equation by doping, helps to estimate and analyse the relative impact of the process factors which are not directly determined and the model is validly verified through a graphical plot of predicted versus actual values of the experimental studies. Study on Fe-removal from eutectic Al-Si alloys of metal mould casting and the resulting significant microstructural improvement is an effort in developing Fe-free Al-Si alloys from scraps for ingots applications and component casting. Fe-free Al-Si alloy is ensured by practical doping experiments and by reasonable prediction of the %Fe removed, the service properties can be reliably determined.

2. Materials and Method

Detailed Fe removal experiments from Al-Si alloy with Mn as the correcting element have been performed by melting of a eutectic Al-Si alloy in an electric furnace of controlled temperature (800°C) with steel crucible and solidified by pouring into metallic mould achieved with gravity after melt fluxing and constant superheating. In this, the charge is melted to achieve close control of metal composition with low melting losses and the avoidance of gas contamination and non-metallic inclusions [14]. The final and initial contents of Fe were confirmed using analytical technique and equipment. The melt of the binary Al-Si alloy and the alloy further alloyed with 0.85, 1.7, 3.4 and 5.1% wt of Mn are obtained, dissolved and homogenised completely by stirring for efficiency in mixing of the fully molten Al-Si alloy before casting by pouring and solidification in metal mould. Weighed filling from the cast specimens were prepared by standard method and analysed for Fe content using Atomic Absorption Spectrometer (AAS) technique to determine the amount of iron present in the cast alloys. The results of the analysis is further analysed using Design-Expert 9 (DX9-04-1 OneFactorRSM) software.
Table 1: Iron content of the studied Al-Si alloys.

| S/N | Alloy Composition | Iron Content, % | Amount of iron removed, % | Deviation from Fe critical level (0.78%)* |
|-----|------------------|----------------|---------------------------|------------------------------------------|
| 1.  | Al-Si            | 1.70           | 0.00                      | + 0.92                                   |
| 2.  | Al-Si + 0.85% Mn | 0.36           | 1.34                      | - 0.42                                   |
| 3.  | Al-Si + 1.7% Mn  | 0.38           | 1.32                      | - 0.40                                   |
| 4.  | Al-Si + 3.4% Mn  | 0.48           | 1.22                      | - 0.30                                   |
| 5.  | Al-Si + 5.1% Mn  | 0.40           | 1.30                      | - 0.38                                   |

2.1 Model formulation

Experimental results obtained from the investigation in table 1 are applied to model the %Fe removed and analysis made using Design Expert software (DX9-04-1-oneFactor RSM). The model equation which predicts %Fe removed as a cubic function is expressed as:

\[ \% \text{Fe removed} = +1.24 - 0.11 \times A + 0.084 \times A^2 + 0.094 \times A^3 \]  
(1)

%Fe removed = +1.30700+0.095882* Al+0.084* A^2 +0.094* A^3  
(2)
in coded and in actual forms respectively where,

A, A^2, A^3 are significant model terms.

2.2 Boundary and initial conditions

The initial Mn content ranged from 0.85 - 5.1%wt contents, furnace and temperature is controlled as well as, mixing of melt by stirring rod at regular time, constant super-heating of melt and holding time, alloy casting at 720 oC, high cooling rate and loss of metal to sludge removal assumed to be less than 5% The evaluated critical Fe level for the Si content of the as-cast Al-Si alloy is 0.78% and the Mn content is 96% pure. Standard specimens were prepared and tested at room temperature. The derived model equation is one-factorial in nature because the predicted %Fe removed for an Al-Si alloy depend on only one factor; Mn content.

2.3 Model validation

The derived model equation is validated by evaluating the model predicted values of %Fe removed and plotting them against the corresponding values obtained from the Fe removal experiments conducted (fig. 2). The result of normal probability plot of the studentized residuals to check for normality of residuals is reported. All the points on the normality plot are seen to match very nicely and the test for departure from normality is found to be insignificant (Design Expert 9). The validity of the derived model is further confirmed by the extremely low p-value (0.0043) obtained from the analysis of variance (ANOVA) for Response Surface Cubic model, which indicates a highly significant advantage. Thus comparison between the model-predicted values of %Fe removed and respective corresponding experimental values show a low and negligible deviation from the model results. The degree of alignment of these values is indicative of the proximate agreement between both experimental and model-predicted values.

3. Results and discussion

The results obtained from the study are shown graphically in figs. 1 and 2. Post ANOVA statistics and Details on model coefficients are presented in tables 2 and 3 respectively. Design-Expert 9 reports that the outcome for the model and model terms are statistically significant. The confidence interval is taken at 95% with the level of significance, P at 5% or 0.05 the software further reports. The dotted lines shown in fig. 1 represent the 95% confidence band on the mean prediction at any given Mn content. From the ANOVA, result parameters show that the Model F-value of 52.81 implies the model is significant. There is only a 0.43% chance that an F-value this large could occur due to other factors.

Values of "Prob > F" less than 0.0500 indicate model terms are significant. The extremely low p-value indicates a highly significant advantage.

Values greater than 0.1000 indicate the model terms are not significant.

Table 2: Post-ANOVA statistics (Design Expert 9)

| Std. Dev. | R-Squared     | Adeq Precision | Pred R-Squared |
|-----------|---------------|----------------|----------------|
| 0.010     | 0.9814        | 15.875         |                |
| Mean      | 1.30          | Adj R-Squared  | 0.9628         |
| C.V. %    | 0.77          | Pred R-Squared | N/A            |
| PRESS     | N/A           |                |                |
The model “R-Squared” of 0.9814 is in reasonable agreement with the “Adj R-Squared” of 0.9628; i.e. the difference is less than 0.2. The Standard Deviation at 0.010 is much lower from the model and insignificant. The variance inflation factors (VIF) – a measure of factor collinearity is also at acceptable significant level. The observation of higher VIF values for A and A^3 model terms are attributed to higher standard error recorded.

### Table 3: Details on model coefficients

| Factor          | Coefficient | Standard Error | 95% CI Low | 95% CI High | VIF |
|-----------------|-------------|----------------|------------|-------------|-----|
| Intercept       | 1.24        | 6.831E-003     | 1.22       | 1.26        |     |
| A-Al-Si+%Mn     | -0.11       | 0.022          | -0.18      | -0.041      | 21.35 |
| A^2             | 0.084       | 8.959E-003     | 0.056      | 0.11        | 1.06 |
| A^3             | 0.094       | 6.831E-003     | 0.023      | 0.17        | 21.34 |

The model equations in terms of coded and actual factors have been derived as:

\[
\% \text{Fe removed} = +1.24 - 0.11 \times A + 0.084 \times A^2 + 0.094 \times A^3 \quad (1)
\]

and

\[
\% \text{Fe removed} = +1.30700+0.095882\times \text{Al-Si+}\%\text{Mn}-0.068512\times\text{Al-Si+}\%\text{Mn}^2+9.77000E-003\times\text{Al-Si+}\%\text{Mn}^3 \quad (2)
\]

And both equations can be used to make predictions about the response for given levels of Mn content. The coded equation in particular is useful for identifying the relative impact of the factors by comparing the factor coefficients (Design Expert 9). It is evident from the derived model equation (2) that %Fe removed is not only dependent on Mn contents but that it varies cubically with %Mn in the investigated alloys. The coefficient estimate indicates that the cubic model term (A^3) exacts the maximum influence on %Fe removed of all the model terms (mean, linear, and quadratic) observed. The cubic model produces the highest coefficient estimate as seen from the details on model coefficients in table 3 but with lowest standard error of all the models observed.
Fig. 2: Predicted versus actual response

The model graph of fig 1 reveals that %Fe removed varies as a function of %Mn indicating that %Fe removed exhibited an overall initial decreasing trend with increasing Mn addition from 0.85 to 3.4 wt% and exhibited a substantial sharp increase at the level of Mn content of 5.1 wt%. This shows that Mn is a more effective Fe removing metal at both lower and higher levels of Mn contents. A further observation of fig. 1 however, indicates that the %Fe removed which is predicted in the study is maximum in 0.85 wt% Mn or Mn/Fe of 2/1. Analysis of Table 1 also shows that the reduction in Fe content as a result of Mn introduction ranged from 1.7 wt% to an average of 0.4 wt% or 76% Fe removed. This value is comparable to the numbers reported for %Fe removed by other authors in Fe removal experiments [7]. From the analysed experimental results, it is found that the concentration of Al in the eutectic alloy per weight of %Fe increased from 51 wt% in the initial master alloy to about 205 wt% in the Fe corrected cast alloys assuming low melting losses. Thus the Fe removal fraction is quite high, suggesting that the as-cast Al-Si eutectic alloy has been made much lighter and well reusable as a result of the reduction in Fe content which gives it a higher strength to weight ratio. The reduction in Fe content and thus with near constant Si content makes higher the strength, ductility and reduction in area (%) of Al-Si alloys whereas the hardness diminishes [13].

4. Conclusion

The model equation is obtained to predict the %Fe removed during Fe removal processing with Mn. And since other Fe removing elements such as Co, Ni, and Mo have similar physicochemical characteristics with Mn, it gives clue to formulate a predictive model for %Fe removed with those other elements.

The derived model shows that equation for evaluating %Fe removed from Al-Si alloys could be validly derived. The equation is important because it is a general relationship which is applicable to evaluation and analysis of %Fe removed from Al-Si alloys. Values for %Fe removed may be evaluated for different Mn contents within the given appropriate boundary.

The derived model is found to be a response surface cubic model which can predict the %Fe removed in an Al-Si alloy with a maximum standard deviation of 0.010 which is quite within the range of acceptable deviation limit for experimental results.
Acknowledgment
The authors are very grateful to the authorities of CIFA Laboratory, Enugu for the technical support and to Design-Expert 9 for the applied software for analysis of results and model derivation.

References
[1] Nnuka, E.E. Recycling of secondary aluminium alloys. Proceeding of the 1989 Annual Conference of the Nigerian Society of Engineers, Abuja 1989; pp 49-54.
[2] Nwankwo, N. E. (2015). Metallurgical techniques for improving the mechanical and physical properties of Al-Si alloys. Ph.D Thesis. Metallurgical and Materials Engineering Department, Nnamdi Azikiwe University, Awka.
[3] Oluwadayo, F. A and S. O. Ogundele (2014). Mathematical modelling to study heavy metal pollution and effectiveness of commercial heavy metal chelators. National conference on Engineering for sustainable development. Faculty of Engineering, Nnamdi Azikiwe University, Awka pp72
[4] Nwankwo, N. E. and E. E. Nnuka. The effect of iron removal from Al-Si alloys and sodium refinement of the structure. International Journal of Innovation in Science and mathematics 2014. www.ijism.org.
[5] Nwankwo, N. E. and E. E. Nnuka. Mechanism of iron removal from Al-Si alloys by metallic dopants. International Journal of Innovation in Science and Mathematics 2014. www.ijism.org.
[6] China Papers. Com. Effect and mechanism of iron removal from aluminium melt by Boron compounds. 2010 pp 1486.
[7] Lifeng Z. and L.N. Damoah. Current technologies for the removal of iron form aluminium alloys. The Mineral Metals and Materials Science 2011pp 757-762.
[8] Nnuka, E. E. Agbo U. J. E and S. I. Okeke. The effect of the modification of the structure of iron and silicon on the mechanical properties of Al-12% Si alloys. Journal of Engineering and Applied Science. NAU; 2007; 3 (1 and 2): 86-94.
[9] Nwoye, C. I., Obasi, G. C. Mark, U. Inyama, S. and Nwankwo, C. C. Model for calculating the concentration of leached iron relative to the final solution temperature during sulphuric acid leaching of iron oxide ore. New York sc. Journal 2009; 2(3): 49-54.
[10] Dieter, G. E. Mechanical Metallurgy, Mc Graw-Hill series in Materials Science and Engineering. Pp263.
[11] Nwoye, C. I., Agu, P. C., Mark, U., Ikele, U. S., Mbuka, I. E., and Anyakwo, C. N. Model for Predicting Phosphorus Removal in Relation to Weight of Iron Oxide Ore and pH during Leaching with Oxalic Acid. Inter. J. Nat. Appl. Sc., 2008; 4(3): 292-298.
[12] Nwankwo N. E. Nwoke, V. U. and E. E. Nnuka ( ). Effect of Ni additions on the microstructure and mechanical properties of Fe-based chill Al-Si cast alloys for production of pistons for automobile engine applications. International Journal of Scientific Research Engineering Technology 2015; 1 (2).
[13] Henkel, D and A. Pense (2002). Structure and properties of engineering materials. McGraw Hill Higher Education Publishers. New York pp 285.
[14] Beeley, P. R. (1972). Foundry Technology. Butterworth & Co Publishers Ltd. London. pp. 395.