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INFLUENCE OF SODIUM CHLORIDE MODIFIER ON THE PROPERTIES OF ALUMINIUM-SILICON ALLOY

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Abstract

Solidification of aluminium-silicon alloy produces coarse eutectic microstructures consisting of large and brittle plates in aluminium matrix. This result lowers the mechanical properties of alloy. Chemical modification was applied to improve the properties of aluminum-silicon (Al-Si) alloy. The Aluminium-silicon alloy was developed and modified with sodium chloride salt using sand casting technique. The amount of salt used was calculated stoichiometrically. The percentage variation of sodium content in sodium chloride was 0.005%, 0.01%, 0.015%. Aluminium ingot, aluminum-silicon ligand and magnesium metal were melted in the furnace at varying temperatures (750^{o}C, 800^{o}C and 850^{o}C) to form the hypoeutectic alloy conforming to AA354 alloy. The modified salt was introduced into the molten metal, mixed and then cast into molds. The cast samples were subjected to Characterization such as microstructural analysis, X-Ray Defraction and thermal conductivity analysis and mechanical properties such as tensile, impact and hardness tests. The X-Ray Diffractometer analysis was conducted on the cast sample to determine the grain refinement and the crystallinity of the modified alloy. The microstructure revealed the brake down. The tensile strength of the unmodified alloy was 80.54MPa. The addition of sodium chloride was discovered to have increased the tensile strength to 189.51MPa. The hardness value increased from 60.87HRB for the unmodified to 82.1HRB for sodium chloride modified alloy. The impact strength of the alloy decreased from 2.03J for the unmodified alloy to1.68J for the modified alloy. The modifying salt (NaCl) changed the eutectic structure of the aluminium-silicon alloy. The changes in the structure were reflected in the outcome of the various tests conducted on the developed samples. The modified aluminium-silicon alloy was used successfully for the casting of an automobile brake disc.

Keywords: *Tensile strength, modification, Aluminium-Silicon alloy, impact strength, characterization*

1. **Introduction**

Aluminium-Silicon (Al-Si) alloys are the predominant alloy used for light metal casting components. This is due to their low weight, good castability low cost and favourable mechanical properties [1]. Aluminium-Silicon alloys or the matrix are widely used in industrial applications such as automobile, aviation, marine and agricultural. An aluminium-silicon (Al-Si) alloy has a composed microstructure. For instance, Aluminium-silicon alloy is widely used in automotive or aircraft applications due to its high strength-weight ratio since this saves energy and cost of operations. According to Jeong [2], the recent environmental demands in the automotive industry prompt several companies to produce fuel-efficient vehicles using lighter-weight materials. The physical and mechanical properties of the alloy are influenced by its chemical composition and microstructure. However, the as-cast Al-Si alloys have brittle eutectic silicon phases with coarse and plate-like (flake-like) morphology. The sharp ends of the plate-like silicon phase act as stress concentration points which promote crack initiation, and ultimately result in poor mechanical properties. To improve the mechanical strength, Bialobrzeski et al [3] reported that to improve the mechanical properties of the cast Al-Si alloys, chemical, thermal and mechanical modification is employed.

Chemical modification of hypoeutectic aluminium-silicon alloys involves the improvement of properties by inducing structural modification of the normally occurring eutectic. Modification is achieved by the addition of certain elements such as calcium, sodium, strontium, and antimony. Several studies have been conducted on the chemical modification of Aluminium silicon alloy. For instance, Białobrzeski et al [3] modified the aluminium-silicon alloy with sodium utilizing electrolysis of sodium salts. The degree of alloy modification was confirmed through the improvement of the ultimate tensile strength (UTS or Rm) and analysis of the microstructure of the alloy. Also, Martin [4] modified high-performing cast Aluminium Silicon Alloys with sodium and strontium. The concentration of sodium is between 0.005 to 0.01wt% and Strontium levels of 0.02 to 0.04wt%. It was observed that sodium and strontium dissolves readily in the alloy and the mechanical strength of the alloy improved significantly. However, due to very high vapour pressure, a large fraction of sodium boils off when expose to air from the melt resulting in the loss of a significant amount of sodium. On the other hand, finely powdered Strontium metal is sufficiently reactive and ignites when expose to air. These problems have made these efficient chemical modifiers (Sodium and Strontium) difficult to use without adequate training on storage and applications. Hence, there is a need to exploit relatively stable compounds for the modification of Aluminium-Silicon alloy.

This research study focused on the chemical modification of Al-Si alloy using sodium chloride (NaCl) in place of sodium metal and the effect of different casting temperatures (750, 800 and 850 ^{o}C) on the produced alloy was investigated. The microstructure of the as-cast (unmodified) and the modified samples was studied to observe the extent to which the salts can transform the flake-like morphology of the silicon phase to cellulose/fibrous morphology. The morphology of the modified alloy was assessed through a metallurgical microscope. The hardness, impact, and tensile strength tests were performed to assess the level of improvement in the mechanical properties resulting from the structural modification.

2. Materials and Methods

2.1 Materials

The materials required for this research study include Aluminum-silicon (silumin), pure aluminium (wrought ingot cable), and Magnesium metal as presented in Plate 1. The Aluminium-silicon (silumin) was sourced from Zaria aluminium auto shop. Salts of chemical modifiers in the form of sodium chloride were used. The Sodium chloride was sourced from a chemical laboratory in Zaria.

Plate 1. Input charge components

2.2 Alloy Development

Production of molten metal to meet a particular chemical specification requires knowledge of the composition of the final product and the composition of the selected input materials. The composition of the input materials was established through the information from the supplier and chemical analysis in the laboratory using X-Ray fluorescence (X-RF). The chemical composition of the input-charged component is presented in Table 1.This information is used for calculating the charge components to meet the set goal of the product's chemical specification.An electric resistance muffle furnace was employed for the melting of the aluminium alloy. The aluminium ingot was charged into the crucible and inserted into the furnace. The furnace was heated to the melting temperature of aluminium (660 ^{o}C).Then, the silumin was introduced and heated further to melt.Finally, the balance of magnesium was added and stirred to form the alloy. The modifying salts were finally introduced using the parameters in Table 2, and then stirred to a homogeneous composition. The produced melt was treated at different casting temperature as illustrated in Table 2.

Table1. Input charge materials

Input charge components	**Materials Composition (%)**			
	Al	Si	Cu	Mg
Aluminium ingot	99.9	-	-	-
Magnesium powder	-	-	-	99.9
Silumin (Al-Si alloy)	Bal	12.38	3.4	0.46

Table 2. Parameters for the production of the composite

At 750^{o}C casting temperature		Remark
NA1	0.005	0.005% NaCl
NB1	0.01	0.01% NaCl
NC1	0.015	0.015% NaCl
At 800^{o}C casting temperature		
NA2	0.005	0.005% NaCl
NB2	0.01	0.01% NaCl
NC2	0.015	0.015% NaCl
At 850^{o}C casting temperature		
NA3	0.005	0.005% NaCl
NB3	0.01	0.01% NaCl
NC3	0.015	0.015% NaCl

The molten metal was poured into the mould in a steady stream with a crucible close to the pouring basin of the mould. Sufficient time was allowed for the metal to solidify in the mould. the casting was shake-out from the mould carefully and the riser and the gating system were cut-off. Finally, the casting was inspected visually and surface and dimensional defects were observed. The samples were polished using standard metallographic method and etching of the aluminum alloy was performed using Keller's reagent. The optical microscope was used to observe the etched samples and the X-ray diffraction technique was used to examine the phase present.

2.3 Microstructural Examination

Microstructural examination (Metallography) is essentially the study of the structural characteristics or constitution of a metal or an alloy in relation to its physical and mechanical properties. The most important part of metallography deals with the microscope examination of prepared metal specimen. The process of microstructural examination involved sectioning, grinding, polishing, etching and microscopic view of the test sample.

The grinding of samples were performed starting with rough grinding with abrasive paper of 120 grits. This was followed by finer grits of 220, 320, 400, 600, 800 and 1000 in succession.

The polishing was performed according to ASTM E3-11. Polishing was carried out on cloth covered rotating wheels. The etching was performed according to ASTM E3-11. The etching of the aluminum alloy was performed using keller's reagent.

2.4 X-Ray diffraction Analysis of the Al-Si Alloy

XRD patterns of the cast Aluminium-silicon alloy (unmodified and modified) with different concentrations of Sodium chloride modifier were performed using Rigakuminiflex 300 X-ray diffraction machine. The peaks in the pattern were matched using the JCPDS file number 96-101-0925 and could be identified as orthorhombic crystal systems with a lattice parameter as a = 7.76Â, b = 7.9 Â and c = 5.56 Â. The peaks correspond to the ones reported by Hekimoğlu, et al., (2019).

2.5. Thermal Conductivity

The thermal conductivity was performed using Serle's Thermal Conductivity Apparatus, Voltmeter, Ammeter, Thermometer, D.C power supply unit, connecting wire vernier calipers and micrometer screw gauge. The voltmeter was connected across the terminals of D.C power supply unit of the Serle. We appropriately connect the water supply was connected to ensure steady flow of the water round the Serle's Apparatus.

Then the thermal conductivity (k) of the sample was calculated by using

$$K = \frac{VIL}{A\Delta T} \quad (1)$$

where: V = voltage in Volt (V); I= Current in Ampere (A); L= Thickness of the sample in meter (m); A= cross sectional area in meter square (m^2); ΔT= Temperature difference in degree celcius (^oC)

2.6 Impact Test

The impact test was performed on the standard impact test samples conforming to the standard methods of impact testing of aluminium alloys as per ASTM E23. The impact test was performed with the Charpy Hardness tester of the model cat. Nr.412. The impact test specimen was cast to the finish dimension. The test sample has a cross-sectional area of 10mm square with an overall length of 80mm. The notch was carefully machined at the centre of the length of the sample to the depth of 2mm with an angle of 45^o.The test specimen was positioned on the specimen support at the anvil. The pendulum was raised to the latched position while the energy pointer indicator was set at the maximum scale. The pendulum was released from a height at an angle of 150^o. The specimen was impacted by the knife-edged strike at the notched point. The value of the absorbed energy was indicated on the energy scale by the pointer. The results were recorded accordingly.

2.7 Rockwell Hardness Test

The hardness test was performed according to the standard of hardness testing of steel materials as per DINS0103; ISO/R80 and ASTM E18 based on Rockwell Hardness "B" scale for testing aluminium alloy. The hardness was performed with an Indent universal Hardness tester of model 8187.5LKV. The pre-load was applied by bringing the sample into contact with the indenter, by turning the hand-wheel clockwise. The movement of the indenter was displayed by a bar graph, and the correct preload position was indicated at the point where the horizontal bar touches the end of the fixed bar. When this point was reached, an audible sound was heard, and the vertical movement of the indenter was stopped. The rest of the loading cycle was an automatic application. At the end of the load cycle, the hardness number was displayed and resolved to 0.1 units. The result was recorded. This process was repeated three times on the same surface and mean values were recorded as the hardness value on Rockwell b-scale.

2.8 Tensile Test

The tensile strength test was performed per the standard method of testing aluminium products as per ASTM B557M-84. The standard extensometer used is the universal strength testing machine of model WDW-100KN, an advanced electromechanically operating machine with a computer-aided digital indicating system. The cross-sectional area of the tension test specimen was determine by measuring the center of the reduced section of the sample with the aid of digital caliper. The measurement was recorded and computed to obtain the cross-sectional area. The equation 2 was used to determine the cross-sectional area was

$$A = W \: X \: T \tag{2}$$

where A = approximate cross sectional area in mm^2, W = width of the test specimen in mm and T = measured thickness of the test sample in mm.

The gauge length was measured from the reduced section by means of caliper and was recorded. The strain rate of 5mm/min was selected from the several options given on the displayed chart on the computer system.

3. Results and Discussion

3.1 Microstructural examination of the Al-Si alloy

The structural morphology of the unmodified and NaCl-modified Al-Si alloy is illustrated in Plate 2. The microstructural examination of the control (modified) sample in Plate 2(a) revealed the eutectic silicon as coarse plates. The sodium chloride salts modified alloy in Plate 4.1 (b-i) exhibits a typical dendritic structure of aluminium and fine grains of eutectic silicon. According to Honeycombe [5], there is a dislocation source that operates within the metal crystal causing dislocations to move and eventually to pile up at the grain boundary. The pile-up causes stress to generate in the adjacent grain, which, when it reaches a critical value will operate a new source in that grain. In this way, the yielding process is propagated from grain to grain. The grain size determines the distance dislocation in the formation of grain boundary pile-ups, and thus the number of dislocations involved. With large grain sizes, the pile-ups will contain larger numbers of dislocations which in turn cause higher stress concentrations in the neighbouring grains. This phenomenon could be adduced to cause the lower strength accompanying the unmodified alloy relative to the modified ones. The introduction of modifying salts has been responsible for the grain refinement of the eutectic silicon phase in the aluminium-silicon alloy. As a result of the refinement, the number of dislocation pile-ups was reduced. The reduction in the number of dislocation pile-ups leads to lower points of stress concentration which aid in improving the mechanical properties of the modified aluminium-silicon alloy as against the unmodified alloy. The difference in the modification behaviour of the unmodified and the modified alloy influence the characteristics and the mechanical properties of the alloy. The modifying salts (NaCl and $SrCl_2$) changed the eutectic structure of the aluminium-silicon alloy. The changes in the structure were reflected in the outcome of the various tests conducted on the developed samples.

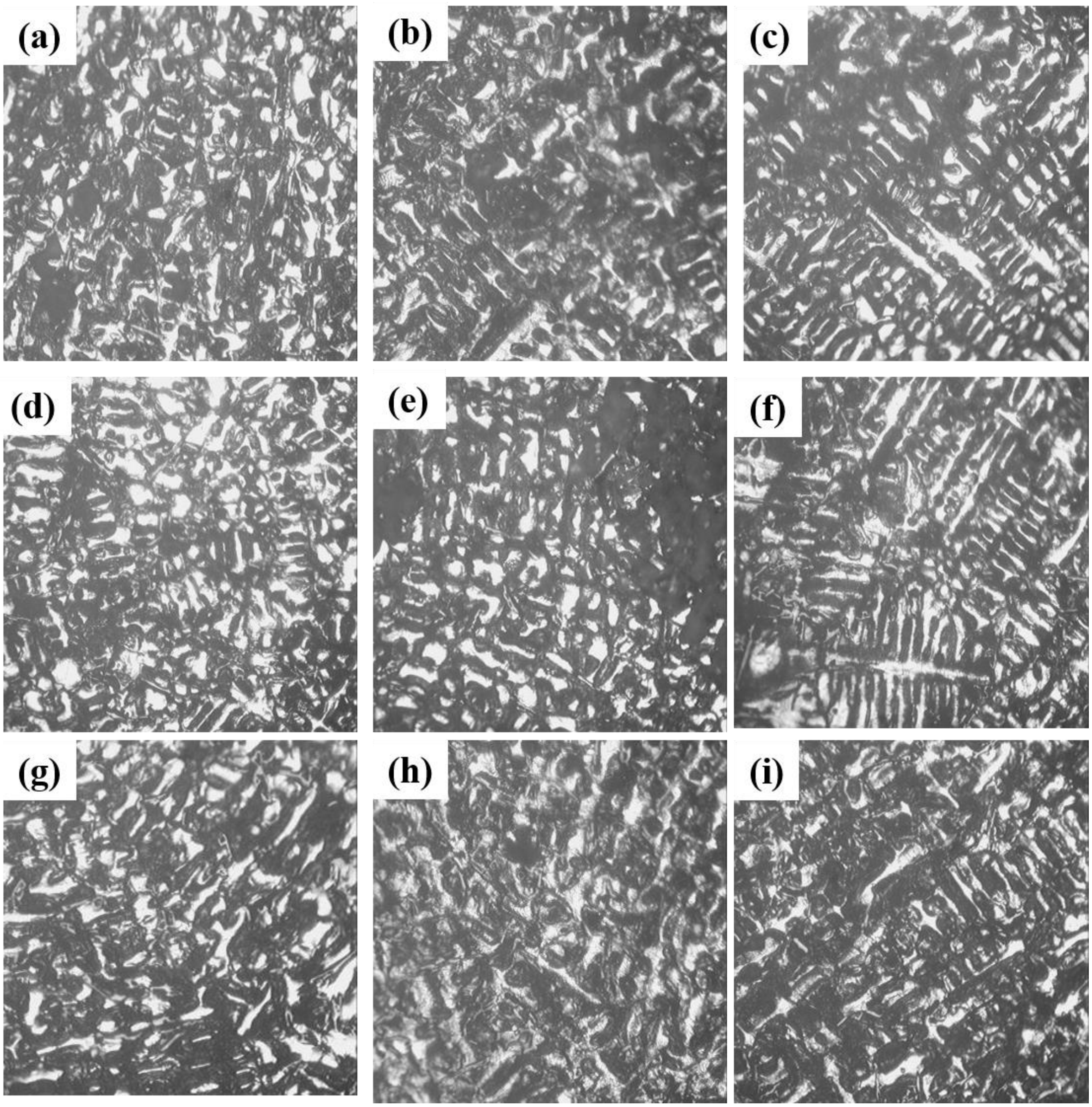

Plate 2 Optical micrograph of (a) Control (b) NA1 (c) NA2 (d) NA3 (e) NB1 (f) NB2 (g) NB3 (h) NC1 (i) NC2

3.2 X-ray diffraction analysis of the Al-Si alloy

XRD patterns of the cast Aluminium-silicon alloy (unmodified and modified) with different concentrations of Sodium chloride modifier are shown in Figure 1. The peaks in the pattern were matched using the JCPDS file number 96-101-0925 and could be identified as orthorhombic crystal systems with a lattice parameter as a = 7.76Â, b = 7.9 Â and c = 5.56 Â. The peaks correspond to the ones reported by Hekimoğlu et al [6]. The patterns show that Aluminium peaks are dominant which was observed at $2\Theta = 39.4^{o}$, 45.5^{o}, and 65.8^{o} corresponding to (131), (202) and (251) miller planes respectively. In addition, minor peaks attributed to the existence of Silicon and the sodium modifier were observed which shows homogeneous dispersion in the Aluminium matrix. The small quantity of sodium chloride added to the alloy does not encompass any new phase by the modification and it's evenly distributed. However, the addition of the sodium chloride modifier resulted in the reduction of the peak intensity ($2\Theta = 65.8^{o}$). The low intensities in the modified alloy could be attributed to the distortion of the atomic planes, which triggered the applied plastic deformation or residual stress resulting in the intensity reduction and peak broadening [7]. The reduction in the intensity of the XRD patterns suggests a grain size refinement [8].

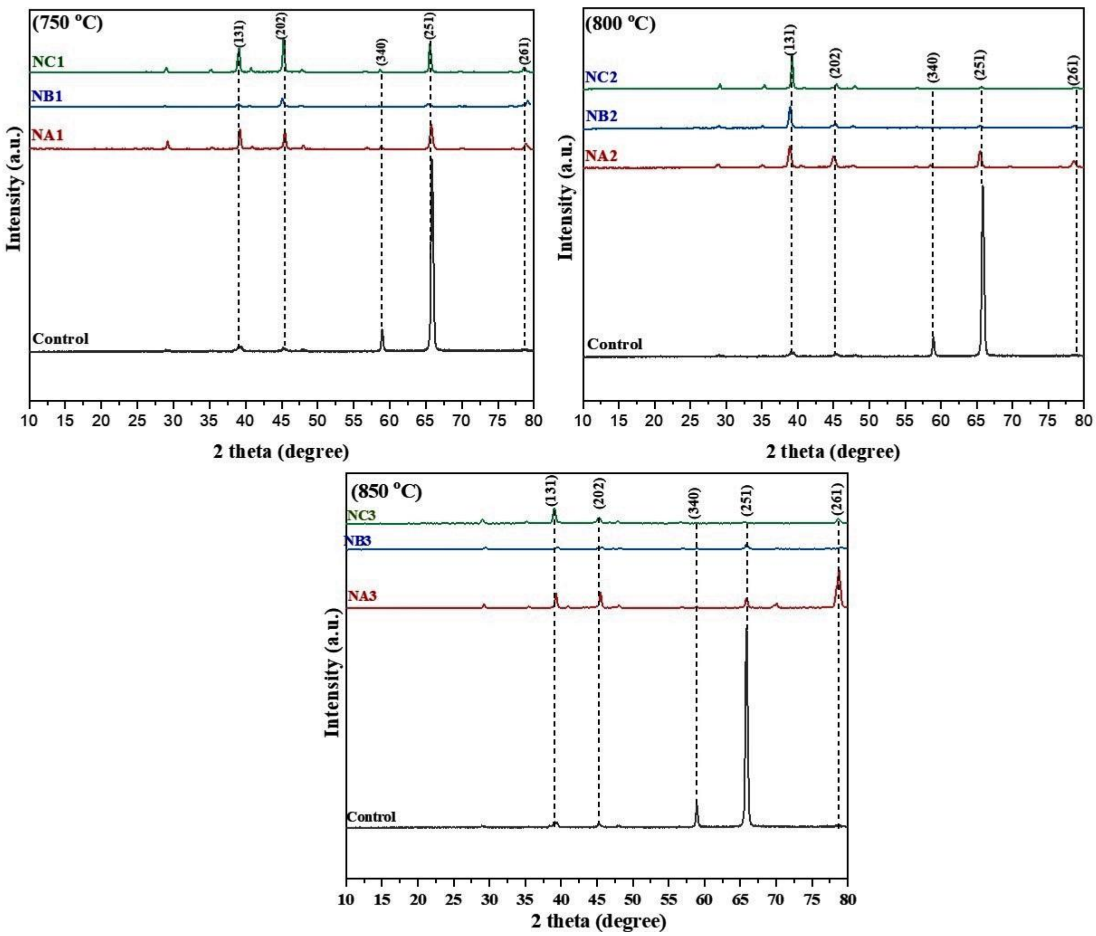

Figure 1. X-ray diffraction spectra of the unmodified and modified (with Sodium Chloride) Al-Si alloy

The average crystallite size decreases with the increase in the concentration of sodium chloride as illustrated in Table 3. This confirms the uniform distribution of the modifier in the matrix, which might act as the site for nucleation. At 750 ^oC, the crystallite size only reduces from 27.9 nm to 27.32 nm with the addition of 0.05 wt.% and further addition (0.01 wt.%) decreases the crystallite size to 19.5 nm. However, the inclusion of 0.015 wt.% sodium chloride led to a sudden increase in the crystallite size. It might mean that the high concentration of the modifier causes sudden growth. A similar trend was seen in the samples heat-treated at 800 ^oC. For the sample heat-treated 850 ^oC, a steady reduction was seen but remained unchanged for samples with 0.01 and 0.015 wt.%. The addition of sodium chloride improves the crystal structure from 89.9 % to values above 90% except for NC1 and NC2 where the crystallinity reduces.

3.3. Thermal Conductivity

The result shows that modified aluminium-silicon alloy has a thermal conductivity of 81.69$Wm^{-1}k^{-1}$ as shown on the Table 4.1. The grey cast iron (3.6-3.9% C) used for the production of brake disc has thermal conductivity of 55W/mk and hardness of 82 HBW hereby indicating that the modified aluminium-silicon alloy has a relatively higher thermal conductivity than the conventional grey cast iron used for break disc.

Table 3. Average crystallite size and crystallinity of the control and sodium chloride-modified samples

Sample code	Average Crystallite Size (nm)	Crystallinity (%)
Control	27.9	89.9
750 ^oC casting temperature		
NA1	27.2	91.6
NB1	19.5	99.6
NC1	29.2	80.6
800 ^oC casting temperature		
NA2	24.0	96.0
NB2	13.7	95.1
NC2	27.7	65.6
850 ^oC casting temperature		
NA3	20.6	99.7
NB3	17.8	99.7
NC3	17.8	99.9

Table 4.4. Thermal conductivity of $SrCl_2$ Al-Si alloy

SC2 Al-Si alloy										
Sample	Area (m^2)	Thickness L (m)	T2º	T1	ΔTº	Volt. (V)	Current (A)	VIL (Wm)	AΔT (m^2K)	K ($Wm^{-1}K^{-1}$)
	0.00 0255	0.004	63.	6	0.	4.2	0.62	0.0104 16	0.00012 8	81.69412

3.4 Tensile strength analysis

The tensile strength of the Al-Si alloy can be improved by the addition of modified Sodium chloride, in addition to the casting temperature effect as confirmed in Figure 2. The ultimate tensile strength and its error bar of the pure aluminium-silicon alloy and modified alloy with different concentrations of Sodium chloride at at different temperatures (750, 800 and 850 ^{o}C) is depicted in Figure 2. The addition of the modifier and the temperature significantly improves the tensile strength of the developed alloy. The ultimate tensile strength of the unmodified sample (control) is 7MPa. The modified alloy with 0.005, 0.01 and 0.015 wt.% of Sodium Chloride, cast at 750 ^{o}C were 131.2, 145.5 and 165.1 MPa with an increment of 39%, 45%, and 51% respectively. The same increment was observed at other temperatures. Therefore, the significant improvement in the ultimate tensile strength might be attributed to the α-al dendrites refinement and the eutectic Si modification [9]. The modifier might have created a strong interface between the matrix and the particles resulting in high strength and stiffness [10]. The optimum ultimate tensile strength of 196.1 MPa was obtained for sample NC2 with 0.015 wt.% of NaCl heated at 800^{o}C. The casting temperature of 800^{o}C could have succeeded in dissociating the salt completely thereby vibrating the sodium (Na being responsible for the modification effect) from the crystal of sodium chloride in the metal. However, raising the sample further up to 850 ^{o}C reduces the UTS. It was observed that increasing the quantity resulted in improvement in the strength reaching the peak at 0.015%Na, 800^{O}C casting temperature.

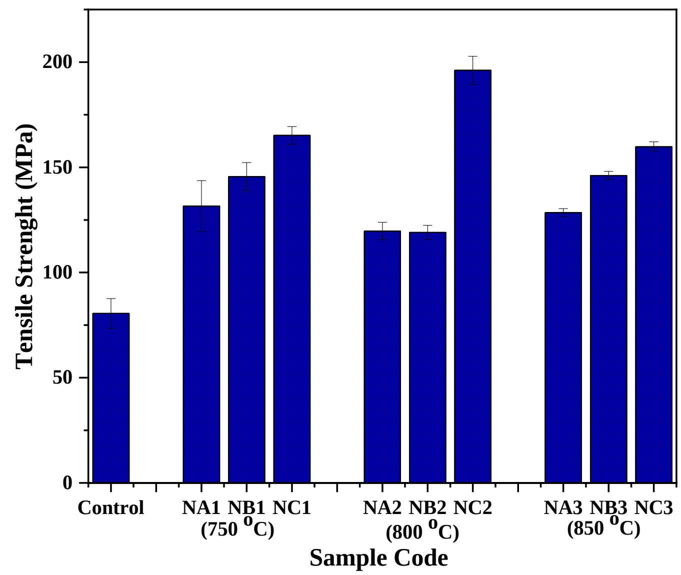

Figure 2. Ultimate tensile strength of the Al-Si alloy unmodified and alloy modified with Sodium chloride

3.5 Hardness result analysis

The hardness of the alloy is controlled by the microstructure. The Rockwell hardness of the Al-Si alloy before and after modification is provided in Figure 3. It is worth noting that the eutectic Si refinement in the modified samples lead to a significant improvement in the hardness. The enhancement in the Rockwell hardness of the alloy might be attributed to the modification effect that is advantageous to the stress concentration decreases. The hardness of the modified alloy falls within 73 to 82 HRB, which is equivalent to over 16% increment compared to the hardness of the unmodified sample (61 HRB). Previous research studies envisaged that the morphology, size and spatial distribution modifier in the alloy could have affected the hardness [11]. Further, increasing the molten alloy temperature from 750^{o}C to 850^{o}C at intervals of 50^{o}C led to an increase in the hardness. The higher process temperature might have influenced the dissociation of the crystals of the chloride salts thereby making available sufficient sodium and strontium for effective modification.

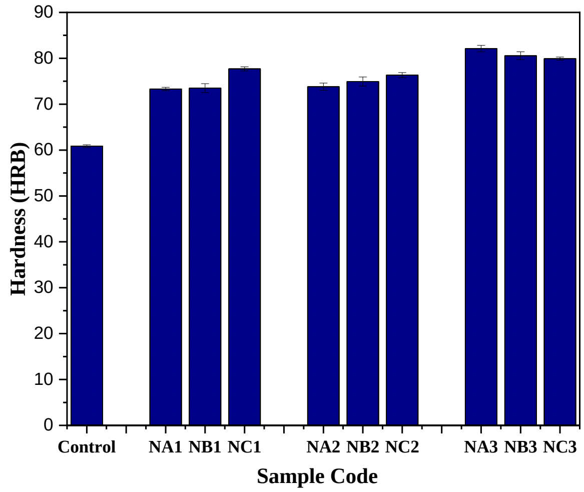

Figure 3. Rockwell hardness of the Al-Si alloy modified with Sodium Chloride

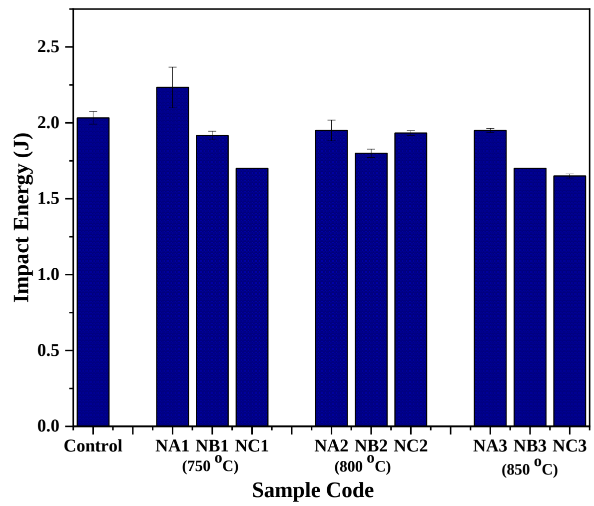

Figure 4. Impact strength of the Al-Si alloy modified with Sodium Chloride

3.6 Impact energy result analysis

An impact test was performed on the test sample to determine the amount of energy absorbed before its fracture or the impact resistance of the test sample. Figure 4 illustrated the impact strength of the Al-Si alloy before and after modification under different temperature regimes. The impact energy of the unmodified sample was 2.03 J. Increase in hardness values resulted in a decrease in impact energy. The impact energy reduces slightly except for NA1, which increases by only 9%. The addition of the least sodium chloride at 750 ^oC gave the highest impact energy at 2.3 J. Increasing the concentration of NaCl and the casting temperature lowers the impact energy. This may be due to the crystal particles of sodium chloride serving as reinforcement agents. The ions simply vibrate in their solid state resulting in a reduction in the impact energy. Generally, high content of sodium chloride led to a 19% reduction in impact energy and a casting temperature of 800 ^oC resulted in a 23% decrease.

4. Conclusion

Hypoeutectic sodium chloride-modified aluminium-silicon alloy was fabricated successfully from aluminium ingot and other alloying elements using the sand casting technique for automobile applications. The microstructure and mechanical properties of the fabricated Al/Si alloy were investigated. The morphology of the unmodified and modified Al/Si alloy was studied using a metallurgical microscope. The following were achieved:

- The microstructural examination conducted on the control sample shows eutectic silicon with coarse grains. However, the addition of the sodium chloride salts causes grain refinement of the eutectic silicon in the aluminium-silicon alloydue to the reduction in the dislocation pile-ups which resulted in a decline in the stress concentration on the modified alloy. This mechanism causes an increase in the mechanical strength of the modified alloy.
- The addition of sodium chloride salt improves the tensile strength of the Al-Si alloy. The ultimate tensile strength of the

unmodified sample was 7 MPa while the addition of 0.005, 0.01 and 0.015 wt.% of Sodium Chloride increase the tensile strength to 131.2, 145.5 and 165.1 MPa respectively. The increase in the tensile strength of attributed to α-al dendrites refinement and the eutectic Si modification. The optimum strength for the sample with sodium chloride was obtained at 0.015 wt.%NaCl then heat treated at 800 ^oC.

- The Rockwell hardness of the modified alloy with sodium chloride falls within 73 to 82 HRB with over 34.7% increment when compared with the unmodified sample with 60.87 HRB. However, the impact energy decreases with an increase in hardness. It is then concluded that increasing the concentration of the modifier and temperature resulted in a decline in the impact energy
- For the calculated wear rate, the addition of sodium chloride to the alloy decreases the wear rate when compared with the unmodified sample. This is attributed to the transformation of the secondary silicon phase into dispersed globules.

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