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Structural Modification of Sand Cast Eutectic Al-Si Alloys with Sulfur/Sodium and Its Effect on Mechanical Properties

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ABSTRACT

In the present study, the structural modification of sand cast Al-12wt%Si alloy with sulfur/sodium and its effect on mechanical properties were investigated. Different addition levels of sulfur and sodium were used to modify and produce castings of the same shape and size from the alloy. The results indicated that the addition of sodium or sulfur to eutectic Al-Si alloy can modify the Al-Si eutectic morphology from needle-like eutectic silicon structure to fine-scale eutectic silicon structure with significant improvement in mechanical properties of the alloy. The optimum levels of modification by sodium flux (60% NaF and 40% NaCl) and sulfur were found to be 0.6% - 1.0% and 0.02% - 0.05% of the weight of the alloy respectively. The alloy modified with 0.6% Na flux had the best mechanical properties closely followed by the one modified with 0.02% sulfur. Over modification of the alloy with sodium produced over modification band which consisted of aluminum dendrites and coarse silicon particles in the microstructure of the alloy. Increase in concentration of sulfur decreased the degree of fineness of the eutectic silicon structure with significant decrease in mechanical properties of the alloy and this is suggested to be as a result of the presence of a brittle sulfur compound at the grain interfaces of the alloy.

Keywords: Aluminum-Silicon Alloy; Sand Casting; Modification; Morphology; Mechanical Properties

1. Introduction

Pacz [1] discovered modification of Al-Si alloys and since then, experimental studies on modification of Al-Si alloys are still going on till today. This is due to the huge importance of modification in the engineering field of alloy design and production of cast Al-Si alloy components with consistent and superior quality.

The binary Al-Si system is a simple eutectic system with about 12% silicon being the eutectic composition at 577˚C. Al-Si alloys are termed eutectic alloys when silicon content is 11% - 13% of the weight of the alloys. Eutectic Al-Si alloys are used in automobile and aeronautical industries for pistons, cylinders, etc.

The composition of most Al-Si foundry alloys is in the vicinity of the eutectic point in order to take full advantage of its excellent castability, and these alloys normally contain about 50 - 90 vol% (Al-Si) eutectic. Hence, the (Al-Si) eutectic is important in determining the mechanical properties of Al-Si foundry alloys. There is need to understand eutectic solidification and modification mechanism in Al-Si alloys.

In untreated Al-Si alloys, the eutectic silicon phase has brittle, coarse and plate-like (flake-like) morphology. The sharp ends of this plate-like silicon phase serve as stress concentrators and promote crack initiation and propagation, and ultimately result in poor mechanical properties of the alloys. Through the process of modification, this brittle, coarse and plate-like eutectic silicon structure can be transformed to fine fibrous eutectic silicon structure with much enhanced mechanical properties [2-5]. Modification is the process of adding trace amounts of certain elements to an alloy to change the morphology of the phase(s) present and ultimately improve the mechanical properties of the alloy.

Eutectic modification which is modification of a eutectic alloy resulting in morphological changes in the eutectic phase(s) present can be explained by the following theories.

Several theories have been put forward to explain eutectic solidification and modification mechanism in Al-Si alloys. Liu Qiyang *et al*. [6] and Dahle and Hillert [7] suggested that AlP present in Al-Si alloys serve as potent nucleation sites for eutectic silicon. This is thought to be as a result of the similarities between the crystal structures of silicon and AlP. Shankar *et al*. [8] proposed that β-(Al, Si, Fe) intermetallic phases present in the alloys also serve as nucleation sites for the eutectic silicon during eutectic solidification. Crosley and Mondolfo [9] also reported that AlP, existing aluminum dendrites and other unidentified particles present in hypoeutectic Al-Si alloys serve as nucleation sites for eutectic silicon at different degrees of undercooling during eutectic solidification.

Basically there are two classes of theories on the mechanism of modification [6]. They are restricted nucleation theory and restricted growth theory. According to restricted nucleation theory, modifier neutralizes the heterogeneous nuclei of AlP which is a nucleant for eutectic silicon or it reduces the diffusion coefficient of silicon in the melt. This enhances undercooling of the melt before eutectic silicon solidification can take place, thus refining of the eutectic silicon structure occurs. According to restricted growth theories, the adsorption of modifier preferentially takes place on twin re-entrant grooves or growing surfaces of the silicon phase, restricting the silicon growth during eutectic silicon growth, and thus requiring eutectic solidification to occur at large undercooling. This causes the eutectic silicon phase to grow isotropically with a fine fibrous structure rather than anisotropically with a faceted (plate-like) structure. Therefore, modification is usually accompanied by a depression of the eutectic temperature. This morphological transformation to fine fibrous eutectic silicon structure is eutectic modification which is accompanied by enhanced mechanical properties.

An important change that takes place upon addition of modifier to an Al-Si alloy is with the number of twins. Lu and Hellawell [10,11] reported that twin density in unmodified silicon flakes is very low and twin spacing is around 0.4 - 1.0 mm on a typical cross section while twin density is much higher in the modified silicon with twin spacing between 0.005 μm and 0.1 μm, which allows silicon to bend and branch more easily to form a fibrous structure.

Research works have been done on eutectic modification of Al-Si alloys with sodium [12-15] but studies have scarcely been done on eutectic modification of Al-Si alloys with sulfur. In this work sodium in the form of sodium flux (60% NaF and 40% NaCl) and elemental sulfur were used to modify eutectic Al-Si alloys and their individual effectiveness as eutectic modifier analyzed and compared.

2. Materials and Procedures

In the present study, the charge materials consisted of commercial purity aluminum and silicon. **Table 1** shows their individual chemical compositions. Degasification of the melt was done with $MnCl_2$. Sodium flux (60% NaF and 40% NaCl) and elemental sulfur in powder form were separately used to modify the alloys.

Al-12wt%Si alloy was prepared from the above charge materials in a clay graphite crucible in an induction furnace and the melt was held at 750˚C. After degassing with manganese chloride ($MnCl_2$), sodium flux (60% NaF and 40% NaCl) or sulfur powder duly wrapped in aluminum foil was added to the melt for modification. The melt was gently stirred for 30 sec with an alumina plunger after addition of modifier to ensure effective mixing and maximize modification. Melts were held for 5 min and then cast into cylindrical test bars of dimension 30 mm diameter × 175 mm length in a sand mould. Sodium flux (60% NaF and 40% NaCl) additions of 0.2%, 0.6%, 1.0% and 1.4% of the weight of the alloy were made to four sets of castings respectively, and sulfur additions of 0.02%, 0.05%, 0.08% and 0.1% of the weight of the alloy were made to another four sets of castings respectively. One set of castings was not modified which served as the control.

Tensile properties of the alloys were determined from ASTM standard tensile test bars machined from the cast cylindrical bars, in as cast condition using a Universal Testing Machine. Hardness test was carried out on 15 mm diameter × 10 mm long cylindrical test bars machined from the cast cylindrical bars in the as-cast condition using a Rockwell hardness tester. An OLYMPUS optical microscope was used to conduct microstructural analysis on the specimens prepared from the broken tensile test bars to examine the effect of modifier additions on the morphology of the eutectic silicon phase. The surfaces of the specimens were ground with different

Table 1. Chemical composition of the charge materials.

Element	Al	Si	Ca	Fe	Cu	Zn	Mn	Mg	Cr	B
Aluminum	99.71	0.045	-	0.23	0.002	0.006	0.001	0.001	0.001	0.004
Silicon	0.185	99.341	0.082	0.392	-	-	-	-	-	-

grades of emery paper from rough to fine grades. The final polishing was done on a Struers Rotopol-V polishing machine using diamond paste and polishing cloth. The samples were etched with caustic soda solution (1 g sodium hydroxide; 99 cm^3 water) [16].

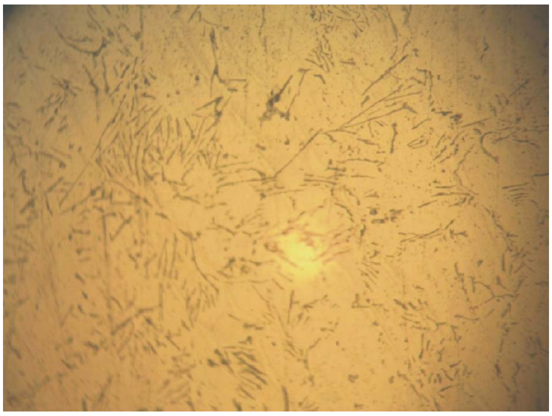
3. Results and Discussion

3.1. Microstructural Analysis

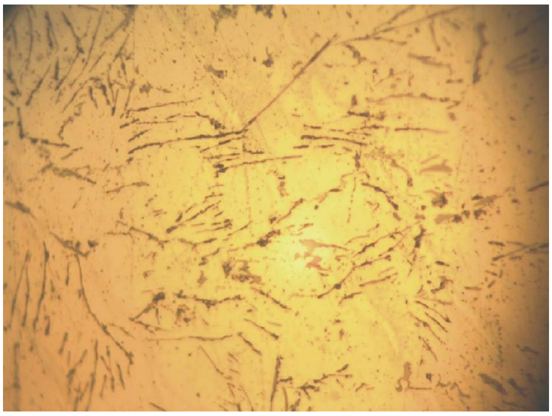
Figures 1(a) and (**b**) are micrographs of unmodified Al-12wt%Si alloy casting in as cast condition showing microstructures in which the eutectic silicon phase is dispersed in the aluminum matrix with needle-like morphology which is actually plate or flake-like in three dimension.

Addition of 0.2% Na flux to the alloy casting results in slight changes in the microstructure of the alloy (**Figure 2**). It can be observed that most of the eutectic silicon is not able to grow into large plates but seems to have been stunted or broken down into smaller sized particles. Though few still exist as large plates, they are not as many and randomly dispersed as those of the unmodified alloy signifying partial modification of the alloy. Addition of 0.02% sulfur to the alloy produces fine eutectic silicon morphology (**Figure 3**). There seems to be the presence of few coarse silicon particles sparsely dispersed in the aluminum matrix, otherwise the needle-like eutectic silicon has been transformed to fine fibrous structure.

Figure 4 which is the micrograph of Al-12wt%Si + 0.6% Na flux alloy casting shows that the microstructure of the eutectic silicon is fully modified. The otherwise flake-like (needle-like) eutectic silicon morphology has been completely transformed to fine-scale eutectic silicon morphology. This observed effect of modification is consistent with the findings of other researchers [2,3, 17-19]. Addition of 0.05% sulfur to the alloy results in a microstructure of fine fibrous eutectic silicon morphology devoid of any needle-like silicon structure (**Figure 5**). The microstructure is comprised of fine fibrous eutectic silicon of fairly uniform size and distribution in the aluminum matrix.



(a)



(b)

Figure 1. (a) Micrograph of unmodified Al-12wt%Si alloy casting (200×); (b) Micrograph of unmodified Al-12wt%Si alloy casting (400×).

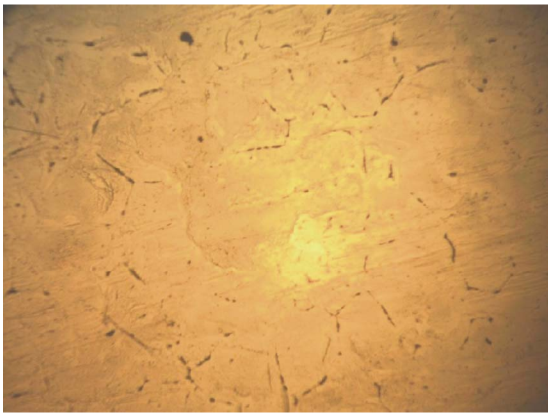


Figure 2. Micrograph of Al-12wt%Si + 0.2% Na flux alloy casting (200×).

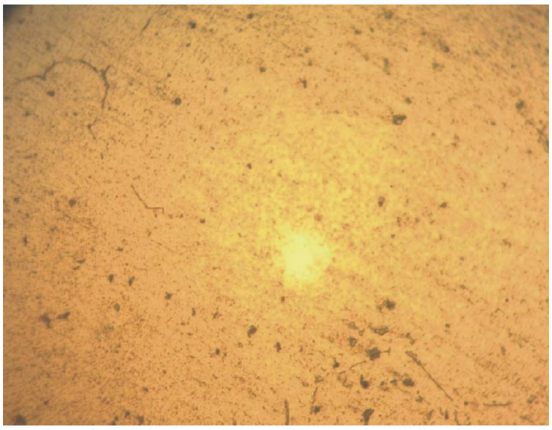


Figure 3. Micrograph of Al-12wt%Si + 0.02% S alloy casting (200×).

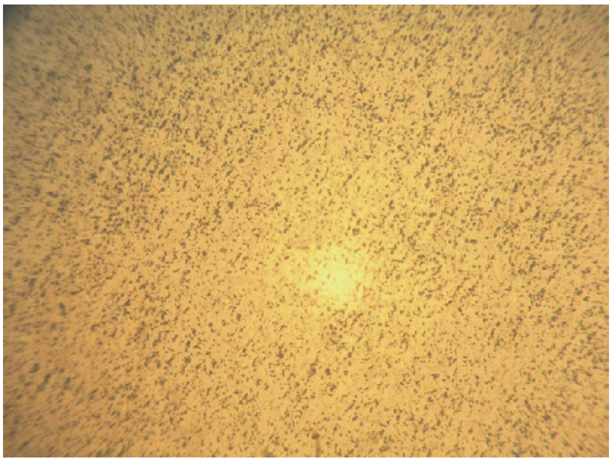


Figure 4. Micrograph of Al-12wt%Si + 0.6% Na flux alloy casting (200×).

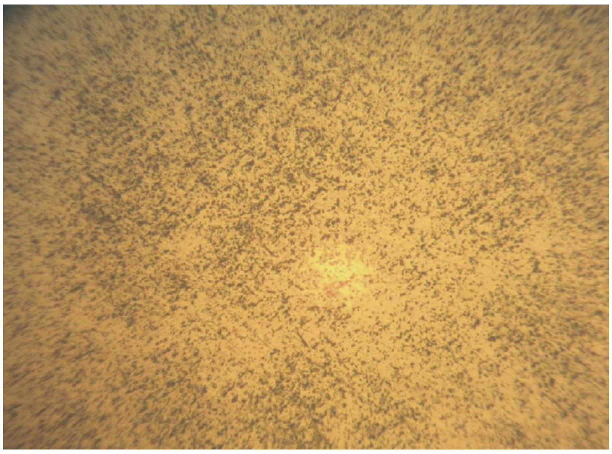


Figure 5. Micrograph of Al-12wt%Si + 0.05% S alloy casting (200×).

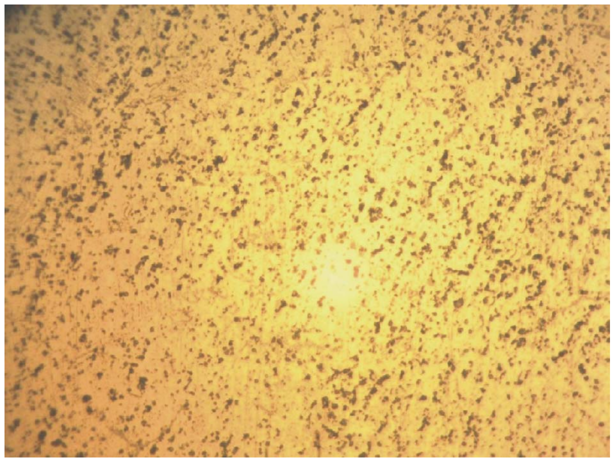


Figure 6. Micrograph of Al-12wt%Si + 1.0% Na flux alloy casting (400×).

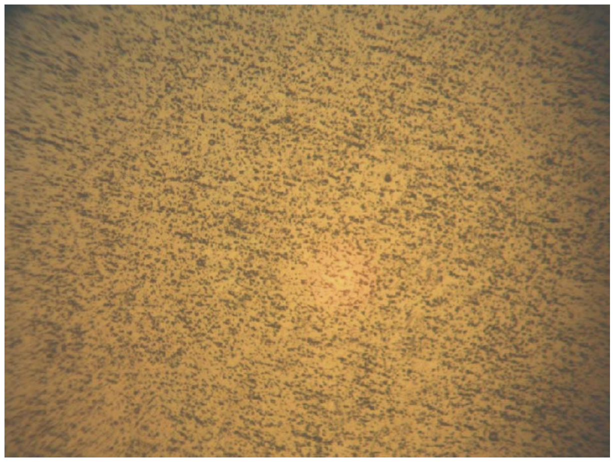


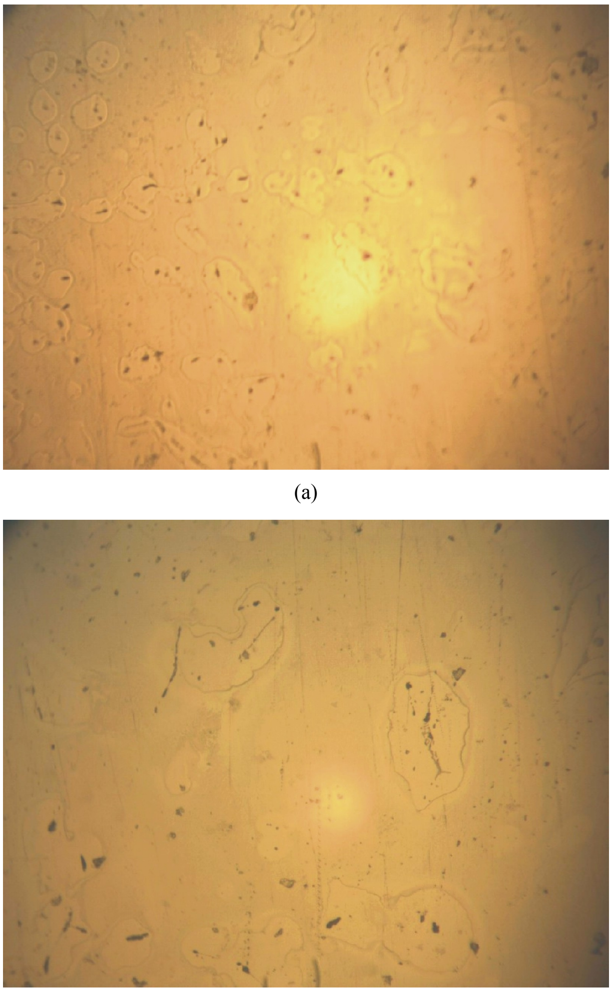
Figure 7. Micrograph of Al-12wt%Si + 0.08% S alloy casting (200×).

Addition of 1.0% Na flux to the alloy also produces fine eutectic silicon structure (**Figure 6**). Modifying the alloy with 0.08% sulfur results in a microstructure of refined eutectic silicon structure though the silicon structure is not as fine as the one obtained for the 0.05% sulfur-modified alloy (**Figure 7**).

Over modification band consisting of aluminum dendrites with coarse silicon particles can be observed on the micrograph of the alloy modified with 1.4% Na flux, implying that the Al-Si eutectic growth has changed to a dendritic growth of aluminum and coarsening of the silicon particles (**Figures 8(a)** and (**b)**). This observation is in agreement with the findings of Kobayashi *et al*. [20] who suggested that the over modification band which appears in the microstructure of eutectic Al-Si alloy modified with sodium consists of aluminum dendrites, coarse silicon particles and at times a ternary compound having chemical composition close to AlSiNa. The micrograph of the alloy modified with 0.1% sulfur shows the presence of fine eutectic silicon and coarse particles that may be silicon particles or other unidentified particles unevenly dispersed in the aluminum matrix (**Figure 9**). This suggests that the optimal modification level of the alloy with sulfur has been exceeded.

3.2. Effect of Modifier Addition on the Mechanical Properties of Al-12wt%Si Alloy

The results of the mechanical properties of the experimental alloy castings in as cast condition are presented in **Table 2**, and **Figures 10-13** show the effect of modifier addition on the mechanical properties (UTS, 0.2% proof stress, percentage elongation and hardness) of the alloy. Modifying the alloy with 0.6% and 1.0% sodium flux of the alloy weight yields the highest UTS of 182 and 176 MPa respectively for the sodium-modified alloys compared to 154.4 MPa obtained for the unmodified alloy. Adding 0.02% and 0.05% sulfur to the alloy produces the



(a)

(b)

Figure 8. (a) Micrograph of Al-12wt%Si + 1.4% Na flux alloy casting (200×); (b) Micrograph of Al-12wt%Si + 1.4% Na flux alloy casting (400×).

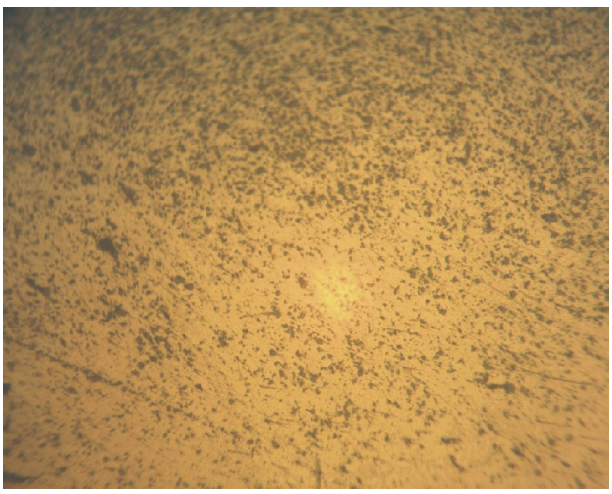


Figure 9. Micrograph of Al-12wt%Si + 0.1% S alloy casting (200×).

Table 2. Mechanical properties of modified and unmodified sand-cast Al-12wt%Si alloy in as cast condition.

Alloy	UTS (MPa)	0.2% Proof Stress (MPa)	% Elongation	Hardness (HRA)
unmodified Al-12wt%Si	154.4	119	3.2	37
Al-12wt%Si + 0.2% Na flux	165	121	4.4	39
Al-12wt%Si + 0.6% Na flux	182	126	10.3	48
Al-12wt%Si + 1.0% Na flux	176	124	8.5	44
Al-12wt%Si + 1.4% Na flux	169	124	6.9	41
Al-12wt%Si + 0.02% S	177.9	126	9.2	47
Al-12wt%Si + 0.05% S	169.4	124	7.1	43
Al-12wt%Si + 0.08% S	161	123	5.2	41
Al-12wt%Si + 0.1% S	160	121	4.6	39

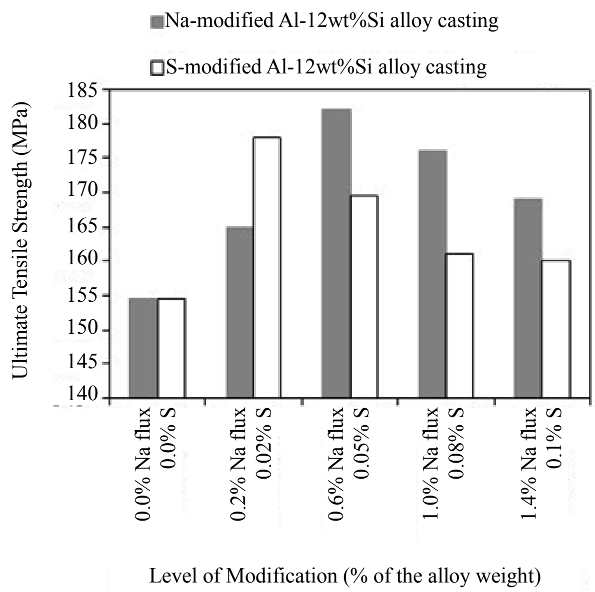


Figure 10. Effect of modification level on the ultimate tensile strength of Al-12wt%Si alloy casting.

highest UTS of approximately 178 and 169.4 MPa respectively for the sulfur-modified alloys.

Comparing the UTS of the sodium-modified and sulfur-modified alloys, it is evident that the 0.6% sodium-modified alloy has the highest UTS closely followed by the 0.02% sulfur-modified alloy. Addition of 0.6% sodium flux and 0.02% sulfur yields the same 0.2% proof stress of 126 MPa while the unmodified alloy has 0.2% proof stress of 119 MPa. Modifying the alloy with 0.6%

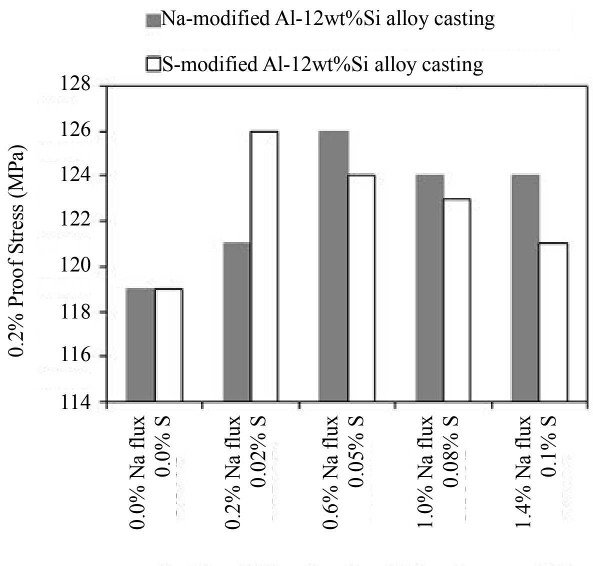


Figure 11. Effect of modification level on the 0.2% proof stress of Al-12wt%Si alloy casting.

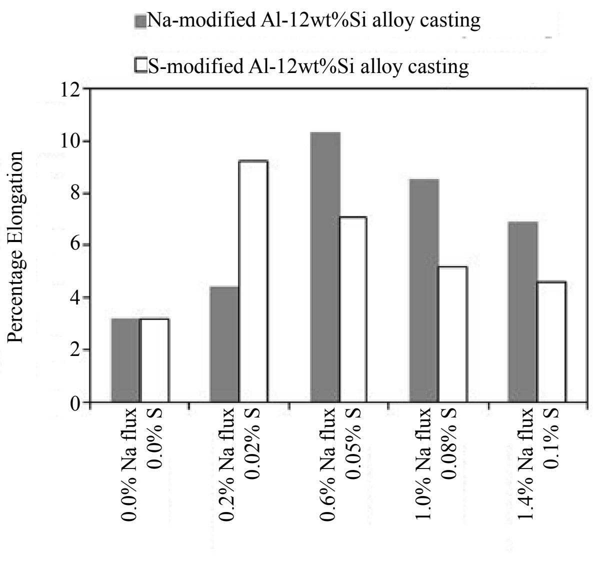


Figure 12. Effect of modification level on the percentage elongation of Al-12wt%Si alloy casting.

sodium flux significantly improves the percentage elongation of the alloy from 3.2% for the unmodified alloy to 10.3%. Addition of 0.02% sulfur to the alloy also produces enhanced percentage elongation of 9.2%. The alloy modified with 0.6% sodium flux has the highest hardness of HRA 48 closely followed by the 0.02% sulfur-modified alloy.

It can be seen from this experimental study that modification of Al-12wt%Si sand-cast alloy with sodium or sulfur improves the mechanical properties of the alloy in

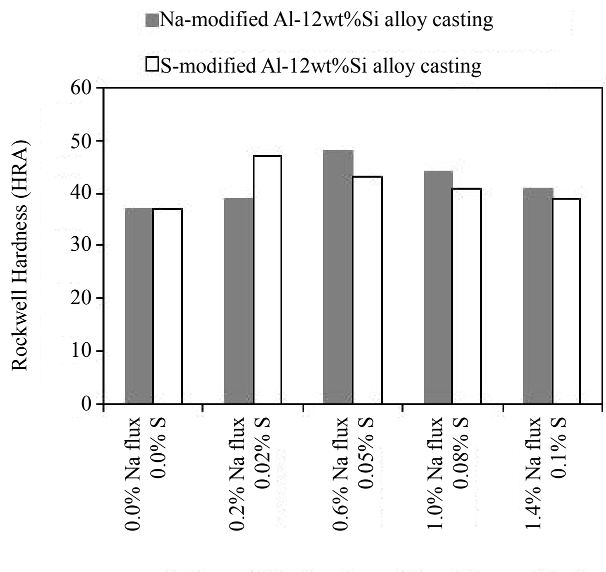


Figure 13. Effect of modification level on the hardness of Al-12wt%Si alloy casting.

terms of the ultimate tensile strength, 0.2% proof stress, percentage elongation and hardness, which is due to the modified eutectic silicon morphology obtained in the microstructure of the alloy. This observation is in agreement with previous reports [2-5]. The reduced mechanical properties of the alloy modified with high sodium concentration of 1.4% Na flux is suggested to be as a result of the over modification band in the microstructure of the alloy which signifies that the optimal level of addition of sodium has been exceeded. It can also be observed that very slight coarsening of the fine eutectic silicon structure occurs as the concentration of the sulfur increases beyond a certain level with attendant significant decrease in otherwise well improved mechanical properties though the mechanical properties still remain better than those of the unmodified alloy. The cause of this significant decrease in mechanical properties despite the still refined eutectic morphology may be the formation of brittle sulfur compound in the alloys which, due to its brittle nature, reduces the mechanical properties of the alloys. This possible explanation could be said to be similar by analogy to that found in steel where the presence of brittle sulphides at the grain boundary interfaces decrease the mechanical properties of the steel [21]. Further studies to support this theory should be considered.

4. Conclusions

The structural modification of sand cast Al-12wt%Si alloy with sulfur/sodium and its effect on mechanical properties have been investigated. The following conclusions can be made from the experimental results and theoretical analysis.

Sodium Modification:

- Sodium can successfully modify Al-12wt%Si sand cast alloy giving it fine fibrous eutectic silicon morphology with significantly enhanced mechanical properties.
- Addition of 0.6% Na flux of the weight of the alloy produced the best eutectic Si morphology and mechanical properties closely followed by addition of 1.0% Na flux to the alloy.
- The optimum level of modification of Al-12wt%Si sand-cast alloy with sodium was found to be 0.6% - 1.0% Na flux of the weight of the alloy.
- Addition of 1.4% Na flux of the weight of the alloy produced over modification band in the microstructure of the alloy that consisted of Al dendrites and coarse silicon particles.

Sulfur Modification:

- Sulfur can successfully modify Al-12wt%Si sand cast alloy and significantly improve its mechanical properties.
- Addition of 0.02% sulfur of the weight of the alloy most significantly improved its mechanical properties closely followed by addition of 0.05% sulfur to the alloy.
- The optimum level of modification of Al-12wt%Si sand cast alloy with sulfur was found to be 0.02% - 0.05% sulfur of the weight of the alloy.
- Increasing the concentration of sulfur beyond the optimal level moderately decreased the degree of fineness of the eutectic silicon morphology but significantly reduced the mechanical properties of the alloy. The cause of this significant decrease in mechanical properties despite the still refined eutectic morphology is suggested to be the presence of brittle sulfur compound at the grain interfaces of the alloy.

Sodium Modification vs Sulfur Modification:

Sodium was found to modify Al-12wt%Si sand cast alloy better than sulfur, producing a more refined eutectic morphology and enhanced mechanical properties.

The optimum levels of modification of Al-12wt%Si sand cast alloys with sulfur and sodium were determined, with attendant improvement in mechanical properties of the alloys modified within these levels. This improvement in mechanical properties of the alloys modified within their optimum levels shows that the overall performance of engineering components cast from such alloys will be significantly enhanced compared to those cast from unmodified alloys.

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