Effect of micro-structural modifier on the morphology of silicon rich secondary phase and strain hardening behavior of eutectic Al-Si alloy

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Abstract. Eutectic Al-Si alloys find their applications in moderate to severe tribological conditions, for example: pistons, casings of high speed pumps and slide sleeves. The higher hardness, so the better tribological properties, are originated by the formation of a silicon rich secondary phase, however, the morphology of the secondary phase drastically influence the toughness of the alloy. Microstructural modifiers are used to control the toughness which modifies the Si rich secondary phase into dispersed spherical structure instead of needle-like network. In the present study, a mixture of chemical fluxes was used to modify the Si phase. The alloy was cast into a sand mold and characterized by scanning electron microscopy, energy dispersive spectroscopy, hardness testing and tensile testing. It was found that the morphology of the Si phase was altered to acicular structure due to the modification process. In comparison, the un-modified alloy contained Si phase in needle-like structure. The effect of modifier was also pronounced on the mechanical properties, where increase of 50% in yield strength, 56% in tensile strength and 200% in elongation occurred. A discernable raise in strain hardening component indicated the improved strain harden ability and formability of the modified alloy.

1. Introduction

While research have been performed recurrently on Al–Si alloys since mid of nineteen century, it is only after 1921 that the alloys have attracted commercial attention after the introduction of “Alpax” a commercial alloy containing ~15% silicon by Pacz [1]. The Al-Si alloy is a simple binary eutectic system with about 12% silicon being the eutectic composition. Al-Si alloys are called eutectic alloys when silicon content is 11% - 13% of the alloys. These alloys are frequently used in aeronautical and automobile industries for cylinders, pistons, guiderails, 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 phase. Hence, the (Al-Si) eutectic phase is important in determining the mechanical properties of these alloys.

In unmodified Al-Si alloys, the eutectic silicon phase has brittle, coarse and needle-like morphology. The sharp ends of this needle-like silicon phase serve as stress concentrators and promote crack initiation and propagation, and ultimately results in poor mechanical properties of the alloy. Through the process of modification, this brittle, coarse and needle-like eutectic silicon structure can be transformed to fine fibrous acicular 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 in the alloy.
Research work have been done on eutectic modification of Al-Si alloys with various modifiers [6-8] but work incorporating eutectic modification of Al-Si alloys along with its effect on strain hardening have hardly been reported so far. In present study modification was carried out for a melt of 1Kg alloy using mixture of fluxes (NaF, KCl and NaCl). The alloy was cast into sand molds and evaluated for its microstructural and mechanical characteristics.

2. Experimental

Generally, eutectic Al-Si alloys have a range of silicon contents i.e. from 7.5 to 12 percent. In present work the proposed chemical composition the alloy is mentioned in Table 1.

| Si   | Mg   | Mn   | Fe  | Cu  | Zn  | Al  |
|------|------|------|-----|-----|-----|-----|
| 8.0 ~ 10.5 | 0.17 ~ 0.3 | 0.2 ~ 0.5 | ≤ 0.60 | ≤ 0.10 | ≤ 0.20 | bal. |
| Achieved | 8.5 | 0.15 | 0.38 | ≤ 0.32 | ≤ 0.21 | ≤ 0.16 | bal. |

To incorporate various alloying additions in the melt of aluminum various addle materials in the form of Al -Si, Al-Mn, and Al -Mg were used. The raw materials used for the melting were cleaned manually. It was assured that any kind of dirt, dross, grease or organic material was not present on the raw materials. After cleaning, raw materials were placed in box oven for pre-heating to eliminate any sort of moisture present in the charge. Any moisture present on the surface of the materials could be a potential source of hydrogen dissolution during melting, which may result in subsequent hydrogen embrittlement. For Al-Mg, the material was heated at 150~200 °C for 20 minutes, while rest of the materials were heated at 25~300 °C for 90 minutes. Pre-heated raw materials were then charged to the electric resistance-heating furnace. Following steps were involved during heating and casting operation:

A graphite crucible was preheated to 600 ~ 700 °C in an electric resistance furnace. At the preheating temperature, pure aluminum was poured in the crucible followed by the addition of melting flux i.e. 0.5 wt. percent of the melt. After complete melting of aluminum, pre-weighed Al-Mn alloy was added. Subsequently, Al-Mg was added. The melt temperature was maintained at 735 ~ 745 °C. To degas the melt, two stage degasing was performed: using Degaser-190 tablets (provided by FOSECO, UK) and vacuum degasing at 10⁻² ~ 10⁻³ mbar pressure. After degasing chemical modification of the eutectic alloy was carried out using a physical mixture of KCl, NaCl and NaF. The modification salt contained 63%NaCl, 12%KCl and 25%NaF and was added in 3% by weight, while maintaining melt temperature between 730 ~ 740°C. After the addition of salt modifier the melt was kept for 10~15 minutes. Meanwhile, the melt was stirred slowly with a steel plunger without breaking the surface of modifier flux. At 710°C the flux was rabbled into the surface of the melt until the exothermic reaction has removed the metal from the flux. The powdery dross was skimmed and alloy was poured into the sand molds.

Energy dispersed spectrometry, optical spark emission and inductively coupled plasma techniques were carried out to analyze the composition of the alloy (table-1).Further, the alloys (with and without modification) were characterized for their microstructural features using scanning electron microscope (SEM) in secondary electron mode. While for mechanical properties Brinell hardness tester was used to determine hardness of the alloys. A steel ball of 2.5mm diameter with a testing load of 30Kg was used for indentation. The value of the hardness was calculated by taking the average of five indentations. An INSTRON universal testing machine was used for tensile properties with a strain rate of 0.02S⁻¹. Two sets of mechanical test specimens (comprising three specimens each) were prepared and tested in accordance with ASTM E8 standard. To determine strain hardening component ASTM E646 standard was followed, according to which:
\[ \delta = k \varepsilon^n \]  
\[ \text{(1)} \]

where, \( \delta \) is true stress, \( \varepsilon \) is true strain, \( k \) is strengthening coefficient and \( n \) is strain hardening component. To calculate true stress (\( \delta \)) and true strain (\( \varepsilon \)) from engineering stress-strain curves, Eq. 2 and 3 were used.

\[ \delta = S(1 + e) \]  
\[ \varepsilon = \ln(1 + e) \]  
\[ \text{(2)} \]
\[ \text{(3)} \]

where, \( S \) and \( e \) are engineering stress and strain, respectively. The seven data points (\( N \)) of engineering stress (\( S \)) and strain (\( e \)) were taken from the region of engineering stress-strain curves between yield point and ultimate tensile strength. Whereas, values of strain rate component and strengthening coefficient were calculated using Eq. 4 to 6.

\[ n = \frac{N \sum_{i=1}^{N} (\log e \log \delta) - \left(\sum_{i=1}^{N} \log e \sum_{i=1}^{N} \log \delta \right)}{N \left(\log e - \frac{\sum_{i=1}^{N} \log e}{N}\right)^2} \]  
\[ \text{(4)} \]

and

\[ k = \exp\{b\} \]  
\[ \text{(5)} \]

where;

\[ b = \frac{\sum_{i=1}^{N} \log \delta \sum_{i=1}^{N} \log e}{N} \]  
\[ \text{(6)} \]

The strain hardening component (\( n \)) and strengthening coefficient (\( k \)) were calculated for three representative engineering tensile curves of the each alloy and averaged out.

3. Results and discussion

3.1 Microstructural Characteristics

The specimens were sectioned from the core area of the castings (both unmodified and modified) and prepared for microstructural investigations. The prepared specimens were intentionally deep etched to reveal the secondary network. Figure 1 shows SEM micrograph of unmodified alloy featuring a typical unmodified secondary silicon phase having needle like morphology. The silicon phase seemed to be disconnected when viewed at low magnification however, at higher magnification, the silicon rich phase appeared as 3-D network (Figure 1b). Additionally, it had flake like morphology (arrows in Figure 1b).

![SEM micrograph of unmodified alloy, a) low magnification and b) at higher magnification](image)

The effect of chemical modification was apparent (Figure 2a), where silicon rich secondary phase was transformed into acicular spherical structure. The otherwise needle-like network structure of secondary
silicon rich phase had been fully transformed to fine eutectic dispersion. The phase appeared as isolated spherical crystals at high magnification (Figure 2b). The spherical dispersed structure was fairly uniform in size and needle-like structures of silicon rich phase were completely transformed after the chemical modification process. Moreover, the dendritic structure of the matrix material (aluminum) was refined after the addition of modifier. The refinement of the matrix dendrites was effected by the uniform and prolific dispersion of the silicon rich phase. Such type of structural refinement could also be achieved by rapid solidification rate, however it is worth mentioning that the mechanism behind the two structural refinement processes (i.e. rapid solidification and chemical modification) are quite different with their effects on mechanical properties.

In modified alloys solidifying at large cooling rates there exist a balance between the rates of heat flow from the liquid to the solid through the interface and released latent heat of fusion, which play a vital role. Aluminum and silicon have large differences in their thermal conductivities and latent heats of fusion i.e. 0.53 & 0.20 cal. cm$^{-2}$. °C$^{-1}$ and 94.6 & 337 cal. g$^{-1}$, respectively. Due to the considerable differences in the thermal conductivities and latent heats of fusion of the two constituent of the alloy, aluminum solidifies rapidly than silicon (figure3a). At higher cooling rate the lead of aluminum becomes larger causing encasement of lagging silicon crystals (Figure 3b & c).

In chemically modified alloys, the impurity induced twinning theory proposed by S. Lu et al [10] explains the mechanism by which chemical modifiers transform the morphology of silicon phase. It is the more widely recognized eutectic modification theory, according to which, chemical modifiers are impurities that poison already growing atomic silicon layers by getting adsorbed onto surface steps and kinks thus preventing the attachment of silicon atoms to the crystal. Furthermore, the adsorbed impurity atoms induce twinning of silicon crystals by altering the stacking sequence of atomic layers as the newly added layers seek to grow around the adsorbed impurity atom.

Figure 2. SEM micrograph of unmodified alloy, a) low magnification and b) at higher magnification

Figure 3. Eutectic solidification in unmodified chill cast Al–Si alloys [9].

3.2 Mechanical characteristics
To understand the effect of chemical modification on the hardness of alloys Brinell hardness tester was used. It was observed that the hardness of modified samples was increased as compared to that of
unmodified alloy. Such improvements in hardness can be attributed to the basic factor of modification of eutectic silicon needle into fine fibrous form. The results of hardness tests are given in Table 2. The mechanical properties of Al-Si alloys in unmodified and modified conditions are shown in Table 2. The yield strength increased approximately 50% from 60 MPa for the unmodified cast alloy to 90 MPa for chemically modified alloy, and similarly tensile strength of modified alloy increased by 56% as compare to unmodified alloy i.e. from 82MPa to 128MPa. Furthermore, the elongation of modified alloy increased approximately thrice than that of unmodified alloy i.e. 0.9% to 2.76%.

For unmodified alloy, it was believed that under loading conditions the needle-like structure of the silicon rich phase not only provided crack initiation but also caused early failure due to the premature fracture of silicon. Hence, compromising on overall strength and ductility of the alloy. In case of modified alloy, where silicon rich phase was present as acicular form, no premature failure of the silicon rich phase occurred, therefore improved strength and ductility were observed[11, 12].

Table 2. Results of hardness and tensile tests

| Specimen     | Yield Strength (MPa) | Ultimate Tensile Strength (MPa) | Elongation (%) | Brinall Hardness (HB) |
|--------------|----------------------|---------------------------------|----------------|-----------------------|
| Unmodified   | 59.7 ±2.4            | 81.6±2.9                        | 0.9 ± 0.1      | 103.1±2.2            |
| Modified     | 89.3 ± 1.8           | 127.6±3.3                       | 2.7 ± 1.4      | 118.7±1.5            |
| Change (%)   | ~50                  | ~56                             | ~200           | ~15                  |

The σ-ε curves of the tensile test were, subsequently, used for determination of strain hardening component and strengthening coefficient of the two alloys (Table 3). It is known that due the morphological modification of the silicon rich phase higher strengths (or strengthening coefficient, k) are achievable. However, it was observed that besides the strengthening coefficient (k), the modified alloy had higher strain hardening component (n) than the unmodified alloy.

Generally speaking, strain hardening component is a measure of increase in strength of the materials due to plastic deformation. Or in other words, as the strain hardening component is calculated from the data points between yield point and ultimate tensile strength; it is the degree of material’s deformability prior to the necking or thinning. It determines how the metal behaves when it is being formed. Materials that have higher n values have better formability than those with low n values [13, 14].

Table 3. “n” and “k” values of unmodified and modified alloys.

|                  | Unmodified Alloy | Modified Alloy |
|------------------|------------------|----------------|
| Strain Hardening Component (n) | 0.17±0.02        | 0.22±0.03      |
| Strengthening Co-efficient (k)  | 511±12           | 988±17         |

4. Conclusions
Eutectic modification of Al-Si alloy was successfully carried out using chemical flux. The needle-like structure of silicon rich phase was completely transformed into acicular fibrous structure. Moreover, the strain harden ability was improved besides tensile strengths and hardness of the modified alloy.

5. Reference
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