Influence of Al-3Ti-0.15C and Ce on Microstructure and Tensile Properties of Al-Si-Cu 319 alloy

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Abstract : In the present research, an attempt has been made to evaluate the effects of addition of Al-3Ti-0.15C (0.05wt%) master alloy with different concentrations (0.1, 0.3, 0.5, 0.8, 1wt%) of cerium (Ce), a rare earth element on microstructure and tensile properties of Al-Si-Cu 319 alloy. Optical microscopy (OM) and field emission scanning electron microscopy (FE-SEM) with EDS analysis was employed to study the microstructural modification and existence of intermetallic compounds. Experimental results show that addition of Ce with up to 0.3wt% increases the tensile properties up to 49.13% as compared to base alloy due to refinement of α-Al and modification of eutectic silicon. In contrast, tensile properties decline above 0.3wt% addition of Ce due to formation of needle like intermetallic compounds. These Ce rich needles like intermetallic compounds suppress the effect of modification, decreasing tensile properties of modified alloy.

1. INTRODUCTION

Hypoeutectic Al-Si-Cu alloys are extensively used in automotive industries among all foundry Al-Si alloys due to their excellent mechanical properties. These alloys provide combination of strength, castability, machinability and good corrosion resistance and used in as-cast as well as in heat treated condition. [1-3]. Microstructure of hypoeutectic Al-Si cast alloy mainly consists of two phases, coarse α-Al dendrites and plate like eutectic silicon. Due to plate like morphology of eutectic silicon phase, mechanical properties like strength and ductility of the alloy are poor [4]. Therefore, simultaneous grain refinement of the α-Al and modification of eutectic silicon particles is needed for improving mechanical behavior of the Al-Si alloy [5].

Researchers have suggested use of Sr, Na, Sb, Ca and P either individually or in combinations, for modification of eutectic silicon [6-9]. Nevertheless, there are certain issues regarding use of these modifiers like porosity formation and over modification in Sr treated alloys [10], toxicity associated with the use of Sb etc. [11]. In recent years, apart from these common modifiers rare earth (RE) elements like Ce, La, Gd, Er, Y, etc. or combination of RE elements are used to modify the eutectic silicon [12-19]. Tsai et al. [13] observed that addition of Ce up to 0.6wt% has no effect on ultimate tensile strength but it improves % elongation of A356 alloy. They have also observed that 1wt.% Ce modified A356 alloy has good modification effect resulting in improved mechanical properties. Ao et al. [14] prepared A380 alloy by squeeze casting with Ce addition. They observed that addition of Ce effectively reduce the size of needlelike β-Al₅FeSi phases from 51µm to 21µm. Li et al. [15] analyzed microstructure and tensile behavior of Al-20%Si hypereutectic alloy. They concluded that size of primary silicon reduced from 94µm to 33µm with increasing content of Ce in Al-20%Si alloy. It also altered the shape of eutectic silicon. RE elements like Ce and lanthanum (La) effectively refine the grain size of α-Al, improve morphology of eutectic silicon and reduce size of SDAS. It also improves
tensile properties in as cast condition and also in T6 heat treated condition of A357 alloy with combined addition of Ce and La [16]. Vijeesh and Prabhu [17] studied effect of combined addition of Ce and Sr on solidification path of Al-8Si-2Cu alloy. They observed improvement in ultimate tensile strength. Addition of Ce increases the nucleation temperature of α-Al and addition of Sr decreased eutectic arrest temperature. Numerous authors have studied the effect of the ternary grain refiners like Al-Ti-B and Al-Ti-C on aluminium and its alloys [20-22]. It has been observed that the refining efficiency of Al-Ti master alloy on α-Al is good but it has lower potential to modify the eutectic silicon particles in Al-7%Si alloy [21]. TiC particles in Al-Ti-C grain refiner are less effective to create the heterogeneous nucleating site as compared to TiB2 particles in Al-Ti-B grain refiner [22]. Therefore researchers have explored quaternary grain refiners like Al-Ti-C-Sr and Al-Ti-C-REmaster alloys for achieving combined effect of refinement and modification [23-27]. Al-Ti-C-Sr master alloy which refines α-Al by inoculating particles like Ti3Al, TiC and modifies eutectic silicon by inoculating platelets like Al7Sr [23]. Some investigations have been made to evaluate the effect of Al-Ti-C-RE master alloy on microstructure and mechanical properties of the Al-Si alloys to achieve refinement and modification [24-26].

There are many reports available on effect of common modifiers like Sr, Sb etc. in Al-Si-Cu alloy but there are few reports available on application of rare earth elements and Al-Ti-C on Al-Si-Cu alloy. 319 alloy is an Al-Si-Cu alloy in family of Al-Si cast alloys which is widely used in automotive industries. The main contribution of present work is to achieve simultaneous grain refinement and modification by adding different wt.% of RE element Ce and Al-3Ti-0.15C along with minor addition of common modifier Sr and study its effect on microstructure and tensile properties of 319 alloy.

2. DEVELOPMENT OF MODIFIED CASTING SAMPLES

Al-3Ti-0.15C, Al-20Ce, and Al-10Ce master alloys were used to get refinement and modification in 319 alloy. Table 1 shows chemical composition of 319 alloy. Ingots of 319 alloy were added to graphite crucible and melted at 750°C in an electric resistance furnace under argon gas environment. After melting of alloy, predefined quantity of Al-3Ti-0.15C and Ce were added to melt gradually. Sr modifier has higher affinity to oxygen, there for a minor amount of Sr i.e. 0.01wt% was added after addition of Al-3Ti-0.15C and Ce. After addition of each master alloy 2 minutes of stirring and 10 minutes of holding time was maintained. Later, degassing of the melt was carried out by hexachloroethane tablet and after removal of slag melt was poured in to the sand mold having cavity size 150×150×10mm3. Total seven cast alloys were developed as presented in Table 2. First alloy (S1) is pure 319 alloy. S2 was developed with addition of 0.05wt% Al-3Ti-0.15C and 0.01wt% Sr in 319 alloy. Remaining five cast alloys were developed with addition of 0.1, 0.3, 0.5, 0.8 and 1wt% of Ce in S2.

Table 1. Chemical composition of 319 alloy

| Element | Si  | Cu  | Fe  | Mn  | Ni  | Zn  | Mg  | Al   |
|---------|-----|-----|-----|-----|-----|-----|-----|------|
| wt.%    | 5.21| 2.97| 0.39| 0.39| 0.30| 0.17| 0.14| Balance |

Table 2. Experimental cast alloys

| Alloy | Chemical composition (wt.%) |
|-------|-----------------------------|
| S1    | Pure 319                    |
| S2    | Al-3Ti-0.15C (0.05)+Sr (0.01)|
| S3    | Al-3Ti-0.15C (0.05)+Sr (0.01)+Ce (0.1) |
| S4    | Al-3Ti-0.15C (0.05)+Sr (0.01)+Ce (0.3) |
| S5    | Al-3Ti-0.15C (0.05)+Sr (0.01)+Ce (0.5) |
| S6    | Al-3Ti-0.15C(0.05)+Sr (0.01)+Ce (0.8) |
| S7    | Al-3Ti-0.15C(0.05)+Sr (0.01)+Ce (1) |
2.1 Microstructural Characterization
Samples used for microstructure analysis were prepared as per ASTM E3 and etched using keller’s reagent. Optical microscopy was performed by Carl Zeiss inverted metallurgical microscope to study the morphology of cast samples. SEM-EDS analysis was performed using JSM 7600F to evaluate intermetallic behaviour and its elemental composition.

2.2 Mechanical Characterization
Specimens for tensile testing samples were prepared as per ASTM E8 standard as shown in figure 1, keeping gauge length 25 mm, thickness 6 mm and gauge width 6 mm. The tensile testing was carried out on universal testing machine (TINIUS OLSEN H50KL) at room temperature.

![Figure 1. Schematic diagram of tensile test specimen (unit: mm)](image)

3. RESULTS AND DISCUSSIONS

3.1 Optical Microscopy
Figure 2 (a-g) shows optical micrographs of experimental cast alloys. It can be observed from the figure 2 (a) that needle like eutectic silicon particles are present in 319 alloy along the α-Al matrix. The thin needle-like structure is transformed into a small rod-like structure on addition of Ce but above 0.3wt% addition of Ce intermetallic compounds which were in block-like and needle like starts forming in the cast samples which accumulated α-Al grain boundries shown in figure 2 (e-g).
Grain size analysis was carried out on biovis material plus software as per ASTM E112. ASTM grain size number (G) of the S1 alloy is 9 and it increases from 9 to 9.5 for S2 alloy. It indicates that numbers of grains/unit area increases from 256 to 362.04 grains/in². In S3, S4, S5 with addition of 0.1%, 0.3% and 0.5wt.% Ce grain size number (G) found to be 10.5, 11.5 and 12 respectively. This indicates number of grains increases with increase in percentage of Ce and it is found to be 2048 grains/in² for 0.5wt% Ce i.e. S5. It can be seen from the figure 3, which represents XRD pattern of 0.8wt.% Ce modified 319 alloy. It shows presence of α-Al, TiC, TiAl₃ and Ti₂Al₂₀Ce phases. According to previous research available on the effect of addition of Al-Ti-C, and Al-Ti-C-Sr master alloys in to the Al-Si alloy melt, particles like TiC, TiAl₃, released from the master alloy in to melt which acts as heterogeneous nucleating sites and hence refines α-Al dendrites while platelets like Al₄Sr and AlTiSr dissolved in to the liquid melt which increases amount of Sr atoms causes modification of eutectic silicon [21, 23, 27].Block-like Ti₂Al₃₀Ce compound in Al-Ti-C-Ce master alloy, decomposes in melt and gives plenty number of free Ce atoms. These free Ce atoms accumulated with other dissociative atoms and forms intermetallic compound which has higher melting point which also act as nucleating site for α-Al.

Figure 2. Microstructure of experimental cast alloys (a) S1 (b) S2 (c) S3 (d) S4 (e) S5 (f) S6 (g) S7
It has been also proven that Ce and other RE element acts as effective agent for simultaneous modification and grain refinement with prolonged modification effect [28, 29]. On the contrary, when Ce content increases above 0.5wt% number of grains/unit area decreases. Number of grains/unit area for 0.8 and 0.1wt% Ce were found to be 512 and 362.04 grains/in\(^2\) due to Ce rich intermetallic compounds. (Refer in section 3.2)

### 3.2 Tensile behavior of modified cast alloys

Figure 4. shows average ultimate tensile strength with 3 samples tested for each experimental cast alloy composition. UTS of unmodified 319 alloy is 116 Mpa and of alloy modified with Al-3Ti-0.15C and Sr is with 128. It can be observed that with minor addition of the Ce i.e. 0.1wt. %and 0.3wt% along with Al-3Ti-0.15C and Sr, UTS increase to 145 Mpa and 173 Mpa respectively as compared to 116 Mpa of unmodified alloy. This is attributed to the modification of the eutectic silicon particles and refinement of the \(\alpha\)-Al. The refinement of \(\alpha\)-Al causes the restriction to movement of dislocation.
On the other hand, with the increasing concentration of the Ce above 0.3wt.% UTS decreases. This is attributed to many reasons like intermetallic compounds, entrapped gases and porosity[30]. As observed in the earlier study, higher concentration of Ce causes the precipitation of large of intermetallic compounds with elements of Al-Si-Cu alloy. The structure of these intermetallic compounds is needle like and it disturbed the modification of eutectic silicon. These brittle intermetallic compounds are thermodynamically stable and distributed around the interdendritic region which produces higher inner stresses resulted reduced tensile properties of alloys [31]. A backscattered electron images with EDS point analysis of alloy with addition of 0.8wt% of Ce was carried out to understand reason behind reduction in tensile strength. Figure 5(a) shows presence of Ce rich intermetallic phases in block like and needle like structure. EDS point analysis of block like structure shows formation of senary Al-Si-Cu-Ce-Ti-C intermetallic phase.

![Figure 5(a)](image)

**Figure 5.** Backscattered electron images with EDS analysis of location marked in image (a). Al-Si-Cu-Ti-Ce-C (b). Al-Si-Cu-Ce-Fe-Ni-C

Figure 5.(b) shows EDS point analysis of needle like structure revealing the formation of septanary Al-Si-Cu-Ce-Fe-Ni-C intermetallic phase containing iron and nickel. Existence of these complex intermetallic phases is attributed to partial dissolution of Ce in to Al-Cu phases, interrupting modification of eutectic silicon [32]. It was also observed that as the concentration of the Ce increases the generation rate of intermetallic compound also increases.
4. CONCLUSIONS

Experimental investigation was carried out to evaluate the effect of combined addition of Al-3Ti-0.15C and Ce on microstructure and tensile properties of 319 cast Al-Si-Cu alloy.

1. Needle like eutectic silicon is transformed to short rod like structure with addition of Ce up to 0.3wt%.
2. Grain size number (G) increases with increasing Ce up to 0.5wt.% indicates refinement of $\alpha$-Al. It decreases above 0.5wt% of Ce.
3. With increasing the amount of Ce, UTS of the modified alloys was effectively increased and then decreased. Decrement in UTS of alloys attributed to the formation of Ce rich intermetallic compounds with alloyed elements.
4. The UTS of the S4 alloy, i.e. 0.3wt.% Ce modified alloy increased to 49.13% from S1 alloy and increased 35% from S2 alloy. Above 0.3wt.% of Ce it decreased to 17.96% from S2 alloy and 9.48% from base alloy.
5. From EDS analysis of 0.8wt% Ce modified alloy, it was found that the Ce rich senary and septanary intermetallic compounds interrupting the modification of eutectic silicon.

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