Effect of alloying elements on thermal stability of Aluminium-Cerium based alloys

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Research Article

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### Materials And Methods

#### Experimental details

#### 2.1 Alloy preparation

Near-eutectic Al-Ce based alloys with composition of Al-12Ce, Al-12Ce-4Si, Al-12Ce-0.4Mg, Al-12Ce-4Si-0.4Mg and Al-12Ce-4Si-0.4Mg-0.25Sr (wt. %) were cast for the present study. Commercial pure aluminium (CPAl) ingot and the following master alloys having purity level 99.7% were used as feedstock: Al-50Si, Al-20Ce, Al-20Mg, and Al-10Sr (wt. %). All the alloys were prepared using resistance type furnace (KANTHAL, SN 1015) and clay bonded graphite crucible. Master alloys of Al-Ce, Al-Si and CPAl together were placed in a crucible and allowed to melt in furnace held at 785 °C. Al-Mg and Al-Sr master alloy were added to the melt at the end with intermittent stirring to ensure chemical homogeneity and minimize oxidation loss. After complete melting, the alloy was degassed with a commercially available degasser, C6. The top oxide layer of the melt was skimmed off before pouring the molten alloy into mild steel mould (1.5 cm diameter and 15 cm height), which was preheated at 300 °C in an air circulated oven. After casting, the cylindrical alloy bars were sectioned using the abrasive cutter to prepare a sample of 2-3 mm thickness for metallography, heat treatment and subsequent studies.

#### 2.2 Metallurgy and microstructure characterization

For microstructural analysis, ASTM E3 standard metallurgical practice was adopted, where final polishing was carried out using 0.01 μm colloidal silica. Keller's reagent was used for chemical etching, whenever required. The FESEM (Field Emission Scanning Electron Microscope) was equipped with a backscattered electron (BSE) and a secondary electron (SE) detector. The attached energy dispersive spectroscopy (EDS) was used for phase specific chemical analysis with 5 kV and 20 kV acceleration voltages. Phase specific EDS analysis was carried out on three random locations for each phase and average composition calculated. For heat treatment studies, samples were polished using alumina slurry up to 12-13 μm surface roughness. Image analysis was carried out using Image J software (version 1.53b) and the systematic manual point count method (ASTM E562) was used for calculation of volume fraction of phases. X-ray diffractometer was equipped with a solid-state detector and operated using Cu-Kα radiation. Quantification of phases and XRD pattern was analysed using Xpert high score (3.0.0) software.
Binary Al-12Ce (Figure 3a) alloy shows the presence of Al (light grey in the matrix) and intermetallic $\text{Al}_{11}\text{Ce}_3$. $\text{Al}_{11}\text{Ce}_3$ is also referred to as $\text{Al}_{4}\text{Ce}$ by some authors [1]. The alloy shows a very faceted eutectic mixture of Al and lathe like intermetallic $\text{Al}_{11}\text{Ce}_3$. Figure 3b shows the XRD pattern of as cast and selected heat treated alloys. The XRD pattern confirms the presence of Al and $\text{Al}_{11}\text{Ce}_3$ phases. From the heat treatment studies (Figure 4), few critical points (encircled) were selected based on high hardness variation compared to as cast alloy. The XRD pattern shows that no new phases form on heat treatment up to 100 hours. The calculated lattice parameters for Al (cubic) and $\text{Al}_{11}\text{Ce}_3$ (orthorhombic) was found to be $a=4.07\AA$ and $a=4.37\AA$, $b=16.63\AA$, $c=8.24\AA$, respectively which are in agreement with reported $a=4.39\AA$, $b=13.2\AA$, $c=10.09\AA$ [5].

Figure 4a and b show heat-treated (300 °C for 10 hours) and as cast microstructure of Al-12Ce alloy respectively. The heat-treated alloy showed coarsening of phases. Heat treatment at 300°C for 10 hours results in a eutectic microstructure that has undergone minor morphological changes. The $\text{Al}_{11}\text{Ce}_3$ phase seems to have spheroidized at many regions and become less intertwined as compared to small and entangled laths in as cast alloy. This suggests a localized minimization of micro constituent surface energy at the eutectic through surface diffusion within the intermetallic and accompanying spheroidization, rather than bulk diffusion through the matrix. In as cast condition, volume fraction of $\text{Al}_{11}\text{Ce}_3$ was found to be 15.5 ± 1.2 % as determined using the systematic manual point count method. Theoretical volume fraction of $\text{Al}_{11}\text{Ce}_3$ from equilibrium phase diagram was found to be 9.45 % [6, 7]. This disparity in volume fraction is due to the non-uniform distribution of intermetallic particle into the Al matrix. The calculated lattice parameters for Al (cubic) and $\text{Al}_{11}\text{Ce}_3$ (orthorhombic) was found to be $a=4.07\AA$, $b=16.63\AA$, $c=8.24\AA$, respectively which are in agreement with reported $a=4.39\AA$, $b=13.2\AA$, $c=10.09\AA$ [5].

Figure 4c shows the heat treatment of binary Al-Ce alloys at three different temperatures of 200 °C, 300 °C and 400 °C for up to 100 hours. Al-12Ce shows microhardness of 510 ± 36.29 MPa as compared to 200 MPa for pure Al [13]. The increased hardness from as-cast to heat treated condition for 300 °C up to 10 hours can be approximated by Orowan strengthening.

An attempt was made to understand the strengthening mechanism in Al-Ce based alloys. Solid solution strengthening, Hall-Petch hardening and precipitation hardening contribute to significant hardening in aluminium alloys. In the presence of precipitates, precipitation hardening can dominate all other hardening mechanisms. Orowan described that precipitation strengthening is a result of precipitate-dislocation interaction in the matrix leading to formation of dislocation loop around the precipitate and increase in yield strength of the material is given by [14]

$$\Delta\sigma = M \left(0.4 + \frac{G}{b} \frac{\ln(\frac{2R}{b})}{\lambda}\right) \frac{f}{\pi \sqrt{(1-\nu)}}$$

(1)

Where $M$: Taylor factor of the matrix, $G$: Shear modulus of the matrix, $\nu$: Poisson ratio of the matrix, $b$: magnitude of Burgers vector, $R$: mean planar precipitate radius given by:

$$R = \frac{\pi}{4} (\lambda)$$

(2)

Where $\lambda$: mean precipitate radius

$K$ and $\lambda$ depends on the distribution of precipitates where $\lambda$ is the effective inter-precipitate distance. For nano dispersed assembly these are given by [15-17]:

$$\lambda = \left(\frac{2\pi}{\sqrt{3}f} - \frac{\pi}{2}\right) \lambda$$

(3)

Where $f$: precipitate volume fraction

The parameters for aluminium in Equation 1are as follows: $M=3.06$ [18], $\nu=0.345$ [18], $b=0.286$ nm [19] and $G=25.4$ GPa [19].

By using equation 1, 2 and 3, increase in Orowan strength for as cast and heat treated condition (300 °C for 10 hours) was estimated to be 103.37 MPa and 112.52 MPa respectively (Table 2). Here $\Delta\sigma/3$ is
approximated as the increment in strength and defined as the difference in microhardness values of as-received alloy and pure Al [20]. Z. C Sims et al. [21] explained the disparity in strength. The neutron diffraction study showed that the load transfer mechanism played significant role in improving the strength. Orowan strengthening mechanism and load transfer mechanism are expected to be active at higher temperatures, although less efficient than at ambient temperature, as dislocation can climb to bypass Al$_3$Ce$_2$ precipitate and the fast creeping Al matrix transfers less load to Al$_3$Ce$_2$ precipitate. An increase in the mean diameter of Al$_3$Ce$_2$ from 142 ± 26 nm in as cast alloy to 175 ± 21 nm in heat treated alloy at 300 °C for 10 hours was observed (Figure 4a and b). However, Eric T. Stromme et al. [22] observed the ageless behaviour in Al-Ce alloys. Although there was coarsening after heat treatment at 300 °C for 10 hours (Figure 3d), Orowan strengthening still dominated in the heat-treated alloy due to increase in volume fraction of intermetallic [23]. The hardness values show a peak for all temperatures studied and then stabilized on prolonged heat treatment for up to 100 hours. This demonstrates that both the hardening mechanisms were active at room and elevated. This study shows the thermal stability of intermetallic Al$_3$Ce$_2$ after heat treatment. The thermal stability of Al$_3$Ce$_2$ can also be ascribed to its high melting point above 1200 °C [24].

### 3.2 Al-12Ce-4Si alloy

Ce reacts favourably with Si and results in formation of a new ternary tetragonal intermetallic Ce(Si$_{1-x}$Al$_x$)$_2$ with x = 0.1-0.9 (Figure 5a). The addition of Si suppresses the formation of intermetallic Al$_3$Ce$_2$(-0.349 eV formation energy per atom). It forms a new stable intermetallic phase Al$_2$Ce (-0.458 eV formation energy per atom) and CeAlSi (-0.585 eV formation energy per atom) which was confirmed by the XRD pattern in Figure 5b [25-27]. As in Al-12Ce alloy, few critical points (encircled) were selected from the heat treatment study of Al-12Ce-4Si alloy, based on large hardness variation from the as cast condition. XRD pattern at those critical points do not show formation of any new phase in Al-12Ce-4Si alloy even after heat treatment for up to 100 hours.

The microstructure of as-cast Al-12Ce-4Si comprises of α-Al, Al$_3$Ce and CeAlSi phase. The intermetallic laths could have formed through an invariant reaction between Al, Ce and Si. The needle like phases (white) persisted even after heat treatment at different temperatures (Figures 6a, b). This shows the high thermal stability of intermetallic phase in aluminium [28-30]. This result can be justified with the higher melting point (more than 1400 °C) of Al$_3$Ce [31].

The effect of Si on yield strength appears to be inconsistent and affects the ultimate tensile strength and work hardening [22]. Therefore, Si addition in Al-12Ce alloy results in marginal change in hardness as compared to binary Al-12Ce alloy. Figure 6c shows the heat treatment studies for Al-12Ce-4Si alloy. After heat treatment at 200 °C for 10 hours, there is a significant increase in hardness. This could be due to the combined effect of dispersion strengthening, solid solution strengthening and load transfer mechanism activated at this temperature. Diffusion data (Table 1) shows that diffusion coefficient of Si at 400 °C is 10$^4$ times higher than 200 °C. Thus, diffusion time for Si at high temperature is much lower and strengthening due to solid solution could be lowered. Though microstructural changes observed at 200 and 400 °C were not significant (Figure 6a and b) but decrease in hardness at 400 °C after 10 hours of aging time was significant suggesting poor thermal stability of the alloy.

### 3.3 Al-12Ce-0.4Mg alloy

Figure 7a shows the as cast microstructure of Al-12Ce-0.4Mg alloy containing eutectic mixture of Al and Al$_3$Ce$_2$ in which Al$_3$Ce$_2$ lathes are firmly interlinked. The XRD pattern also shows Al and Al$_3$Ce$_2$ in as cast alloy. However, upon heat treatment at higher temperatures two new phases, Al$_3$Mg$_2$ and Mg$_2$Al, appear (Figure 7b).<sup>11</sup> This could be due to precipitation of phases in the alloy assisted by higher diffusion coefficient of Mg in Al (Table 1).

The corresponding microstructures of the alloy are shown in Figure 8a and c. Lath-like interconnected Al$_3$Ce$_2$ transforms into discrete particles after heat treatment at 400 °C for 10 hours and becomes more globular as compared to heat treatment at 200 °C for 100 hours (Figure 8c). These alloys showed a 23% increase in hardness at 200 °C for 100 hours, while at 400 °C, there is a 10% decrease in hardness. The variation in the hardness can be inferred from solid solution strengthening, Orowan strengthening and load transfer mechanism. In order to find the contribution of Orowan strengthening microstructural study was conducted on the critical point (Table 3).

| Alloy | Total increment in strength (MPa) = (ΔHV/3) | Orowan strengthening Contribution (MPa) | Load transfer contribution (MPa) |
|-------|---------------------------------|---------------------------------|---------------------------------|
| Al-12Ce (as cast) | 103.37 | 42.27 | 61.10 |
| Al-12Ce (after 10 hours of heat treatment at 300 °C) | 112.52 | 53.07 | 59.45 |

#### Table 2: Calculated increase in strength by Orowan/load transfer mechanism

11. The neutron diffraction study showed that the load transfer mechanism played significant role in improving the strength.
Table 3: Data for area fraction, aspect ratio and increased strength by Orowan/ load transfer/solid solution strengthening mechanisms at critical points

| Alloy                        | Area fraction of Al$_{11}$Ce$_{3}$ (%) | Aspect ratio (length/diameter) of Al$_{11}$Ce$_{3}$ | Total increment in strength (MPa) = $(\Delta$HV/3) | Orowan strengthening Contribution (MPa) | Load transfer + solid solution strengthening contribution (MPa) |
|-----------------------------|----------------------------------------|-----------------------------------------------------|-------------------------------------------------|----------------------------------------|---------------------------------------------------------------|
| Al-12Ce-0.4Mg (after 100 hours of aging time at 200 °C) | 23.07 ± 1.23                        | 9.66 ± 9.50                                       | 179.23                                          | 15.12                                  | 164.11                                                        |
| Al-12Ce-0.4Mg (after 10 hours of aging time at 400 °C) | 21.67 ± 2.63                        | 4.52 ± 4.65                                       | 132.80                                          | 18.84                                  | 113.96                                                        |

3.4 Al-12Ce-4Si-0.4Mg alloy

Addition of 4 wt. % Si and 0.4 wt. % Mg to binary Al-12Ce alloy leads to complete suppression of intermetallic Al$_{11}$Ce$_3$ due to formation of Ce(Si$_{1-X}$Al$_X$)$_2$ with x=0.1 to 0.9, which has lower formation energy (-0.585 eV) than Al$_{11}$Ce$_3$ (-0.349 eV) [25, 27]. Figure 9a show fine eutectic mixture of Al$_3$Si and Al matrix with dispersed Ce(Al$_{1-X}$Si$_X$)$_2$.CeAl$_{1.2}$Si$_{0.8}$ phase is tetragonal with lattice parameters of a = b = 4.24, c = 14.538 Å [34].XRD pattern shows that no phase transformation occurs on heat treatment as compared to as-cast condition (Figure 9b). After the heat treatment, based on high hardness variation, some critical points (encircled) were selected for microstructural study. Figure 10a and b show the micrograph of as cast Al-12Ce-4Si-0.4Mg alloy at 200 °C and 400 °C respectively after 10 hours of heat treatment. Figure 10c shows the heat treatment analysis of Al-12Ce-4Si-0.4Mg alloy. Heat treatment at high temperature (400 °C) results in fragmentation of Al$_9$Si intermetallic lattice and transformation into particle-like morphology. Hardness improves by 33 % at 200 °C for 10 hours of aging time compared to as-cast condition (Figure 10c). This increase in hardness was associated with the combined effect of Si and Mg. The decrease in hardness at 400 °C could be expected due to the loss in solid solution strengthening at high temperature and inactivation of load carrying capacity of the microstructure due to fragmentation (Figure 10b).

3.5 Al-12Ce-4Si-0.4Mg-0.25Sr alloy

Figure 11a demonstrates that further addition of Sr to quaternary alloy refines intermetallic Ce(Si$_{1-X}$Al$_X$)$_2$.Based on hardness values, some critical points (encircled) were selected and XRD study was performed (Figure 11b). Al$_{0.9}$Mg$_{3.1}$ phase was observed in the as-cast condition and disappears after heat treatment possibly due to its lower melting point. Si intermetallic, as observed in the alloy without Sr, is not observed in the alloy with Sr. Figure 11c reported the heat treatment study up to 100 hours for quinary alloy. It shows that Sr addition to quaternary alloy enhances the quinary alloy's room temperature strength. This may be due to increment in solid solution strengthening by addition of Sr. After 10 hours of heat treatment, a significant reduction in hardness was observed at 200 °C. Quinary alloy is characterised by presence of multiple phases and thus making the analysis challenging. The decrease in the hardness can be correlated with less thermal stability and softening and possibly dissolution of Mg$_3$Al phase which is confirmed by the XRD pattern (Figure 11b). For a prolonged heat treatment period, Mg$_3$Al phase disappears.

Conclusion

Microstructure stability of five different Al-Ce based alloys were studied after heat treatment at three different temperatures, i.e., 200 °C, 300 °C and 400 °C. Microhardness measurements were used to ascertain microstructure stability and strengthening mechanisms were discussed. The major conclusions from the work are as follows:

1. Al-Ce binary alloys show thermal stability at all the temperatures studied (200 – 400 °C) due to higher stability of
2. Al-12Ce-4Si is thermally stable at 200 °C but there is progressive decrease in stability at higher temperatures.
3. Al-12Ce-0.4Mg and Al-12Ce-4Si-0.4Mg show thermal stability at 200 °C and 300 °C. The strengthening mechanisms involved are solid solution strengthening, load transfer mechanism and Orowan strengthening.
4. The addition of Sr to Al-12Ce-4Si-0.4Mg alloy fragmented the AlCeSi intermetallic and enhance the room temperature strength. Heat treatment at higher temperatures results in a significant reduction in hardness.

Declarations

Authorship contribution statement

Dheeraj Kumar Saini: Writing original draft. Rahul Gope: Data collection. Animesh Mandal: Conceptualization, supervision, writing-review and editing.

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**Competing Interests:** The authors whose names are listed immediately below certify that they have NO affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript. Author's Name Dheeraj Kumar Saini Rahul Gope Animesh Mandal

**References**
Mechanical properties of Al-Ce alloys at room temperature [2-4]. In binary alloys, Al-12Ce shows better mechanical properties as compared to other binary alloys. In ternary alloys, Mg increases UTS and YS but simultaneously decreases % elongation. 3D printed alloys (manufactured by selective laser melting) show considerable improvement in mechanical properties compared to as cast ternary alloys.
Figure 2

Mechanical properties of 3D printed (manufactured by selective laser melting) Al-Ce-Cu alloys measured at 250 °C [4].

Figure 3

FESEM micrograph of as-cast Al-12Ce (wt. %) alloy showing (a) lattice like intermetallic Al11Ce3 (encircled region showing primary Al11Ce3, (b) XRD pattern

Figure 4

FESEM micrograph for Al-12Ce (wt.% alloy (a) as-cast state shows the globular form of intermetallic in Al matrix (b) spheroidization and coarsening of intermetallic at 300 °C after 10 hours of heat treatment (c) Heat treatment of Al-12Ce alloy up to 100 hours for different time intervals (0, 10, 20, 50, 70 and
100 hours

Figure 5
(a) FESEM micrograph of as-cast Al-12Ce-4Si (wt.%) alloy showing homogeneous distribution of eutectic mixture of Al2Ce and Al (b) XRD pattern of as cast and heat treated alloy

Figure 6
FESEM micrograph for Al-12Ce-4Si (wt.%) alloy in (a) heat treated condition at 200 °C after 10 hours (b) heat treated condition at 400 °C after 10 hours (c) Heat treated Al-12Ce-4Si alloy up to 100 hours for different time intervals (0, 10, 20, 50, 70 and 100 hours)

Figure 7
(a) FESEM micrograph of as-cast Al-12Ce-0.4Mg (wt.% ) alloy, showing entangled lathe and primary precipitation (parallelogram shape of intermetallic Al11Ce3, (b) XRD pattern
Figure 8

(a) FESEM micrograph showing the lathes of intermetallic converting into spheroids particle by minimizing their strain energy through surface diffusion at 400 °C for 10 hours of aging time (b) Heat treatment study for Al-12Ce-0.4Mg alloy for different time intervals (0, 10, 20, 50, 70 and 100 hours) (c) Long lathe-like intermetallic at 200 °C for 100 hours.

Figure 9

(a) FESEM micrograph of as-cast Al-12Ce-4Si-0.4Mg (wt. %) alloy showing homogeneously distributed eutectic of Al and Al9Si intermetallic and dispersed intermetallic Ce(Si1-XAlX)2 (b) XRD pattern.

Figure 10

FESEM micrograph of as-cast Al-12Ce-4Si-0.4Mg (wt.%) alloy showing (a) eutectic and intermetallic CeAlSi after 10 hours of aging at 200 °C, (b) fine and spheroid eutectic after 10 hours of heat treatment at 400 °C, (c) Heat treatment of Al-12Ce-4Si-0.4Mg alloy for different time intervals (0, 10, 20, 50, 70 and 100 hours).
Figure 11

(a) FESEM micrograph of as-cast Al-12Ce-4Si-0.4Mg-0.25Sr alloy, showing and (c) homogeneously distribute phases, (b) XRD pattern, (c) Heat treatment study for Al-12Ce-4Si-0.4Mg-0.25Sr alloy for different time intervals (0, 10, 20, 50, 70 and 100 hours)