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| 1                    | Effects of Thermal Ageing on the Wear Behavior of the Cerium  |
|----------------------|---|
| 2                    | Modified Al-18Si-3.6Cu Alloy  |
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| 18                   |   |
| 19                   | Abstract: In the present investigation, AI-1881-3.6Cu alloy was modified by Cerium (Ce) and   |
| 20                   | that the addition of Co as a modifier changed the membels are of the mineral Si from source with  |
| 21                   | a sharm adda to spherical large acievlar/needlalike subsetia Si into a fibrous state, and dendrite  |
| 22                   | Al phase into round branches with loss interface concretion. After thermal aging the  |
| 23<br>24             | Al phase into found branches with less interface separation. After thermal aging, the microstructure of the modified allow revealed no change in the morphology of the primary Si     |
| 2 <del>4</del><br>25 | nherostructure of the mounted andy revealed no change in the morphology of the primary Si<br>phase. However, a considerable change in the eutectic Si phase and the formation of fine |
| 26                   | precipitates of Al <sub>2</sub> Cu and Al <sub>2</sub> CeSi intermetallics in the matrix Hardness was found to be   |
| 2.7                  | significantly higher in the modified and age-hardened alloys. A Pin-on-Disc wear tester was used  |
| 28                   | to investigate the dry sliding wear behavior of allovs at different loads (10, 20, 30, and 40 N) and  |
| 29                   | 1.0 m/s sliding velocity. The results indicated that the wear rate in the modified allov was lower  |
| 30                   | than the base alloy. Furthermore, the modified alloy after 5hr age hardening demonstrated high  |
| 31                   | wear resistance and improved wear bearing capacity compared to the 1, 3, and 7 hr age hardened  |
| 32                   | alloys.   |
|                      | -   |

Keywords: Hypereutectic Al-Si-Cu alloy, Cerium modifier, Age hardening, Hardness, Wear, Coefficient of friction

#### 1 1. Introduction

2 Aluminum silicon alloys have many industrial applications due to their high strength to weight 3 ratios, good corrosion inhibition, good machinability and wear resistance [1]. Hypereutectic Al-4 Si alloys have low density, high specific stiffness, and high temperature resistance, wear 5 resistance and, low coefficient of thermal expansion and therefore, are used to produce engine 6 block without cylinder liner, and these properties are mostly attributed to the primary Si phase 7 [2]. The Al-Si alloy with approximately 17-18 wt.% Si content shows the best fluidity and, 8 consequently, the best castability. The form, size, and distribution of the primary Si and eutectic 9 phases have a significant impact on the wear properties of the hypereutectic Al-Si alloy [3]. The 10 hypereutectic Al-Si alloy consists of coarse plate/star-like primary Si and needle shape eutectic 11 phases in the dendrite Al matrix. The wear rate at lower loads is less as the coarse primary Si 12 particles serve as load-bearing components [2]. However, under high loading conditions, the 13 coarse primary Si particles break and easily get separated away from the matrix. According to a 14 study [4], the coarse grains are more prone to fracture, which raise the possibility of a third-body 15 wear mechanism since the broken pieces of Si act as an abrasive media. Elmadagli et al. [5] 16 investigated the effect of microstructure (Si wt%, particle size, and morphology) on the wear 17 behavior of Al-Si alloys and reported that increasing the Si content enhanced the transition load, 18 but had only minor effects on the wear rate. A decrease in the aspect ratio or size of the Si 19 particles, on the other hand, increased both wear resistance and the transition load. The 20 hypereutectic Al-Si alloy having 17 wt.% Si content showed better wear resistance [6]. The fine 21 and spherical primary Si phase in the Al matrix was found to increase the wear resistance 22 significantly [1]. Different techniques such as semi-solid processing, electromagnetic stirring, the 23 rapid solidification process, twin roll casting, and ultrasonic vibration have been used 24 successfully to refine microstructures.

Grain refiners (inoculants) introduced during solidification act as nucleation sites for the primary Si particles to promote heterogeneous nucleation [7]. Several rare earth elements have been added in Al-Si alloys to modify the morphology and microstructure of the eutectic Si phase [8-9]. Aluminum phosphate compound (AlP) is formed when phosphorus and aluminum react at high temperatures and this compound has a high melting point (2530°C) and serves as a heterogeneous nucleation site for the primary Si and allows the formation of a larger number of

1 primary Si grains, yielding smaller individual grains [9]. Phosphor is most commonly added as 2 red phosphorus, phosphate salt, or Cu-P master alloy. However, all of these have flaws, 3 particularly the use of P in an Al melt, which brings Occupational Health and Safety (OHS) 4 hazards that can stymie industrial adoption. When AlP comes into contact with moisture, it emits 5 a poisonous and combustible phosphine gas [10]. Modifying elements such as calcium, sodium, 6 strontium, and antimony are used to transform the eutectic Si phase's needle/acicular form into a 7 fine fibrous/laminar form. The rare earth elements such as Yttrium (Y) and Cerium (Ce) have 8 also been found to be effective modifiers, in general, which have a high tendency to alter the Si 9 phase into a fibrous structure, improving its mechanical and wear properties [11]. Zhang et al. 10 [12], reported that the addition of Ce element to Al-18Si alloy resulted in a spherical form of the 11 primary Si and finer lamellar or fibrous eutectic network. However, there was little impact on the 12 eutectic Si that was close to the primary Si particles. According to Li et al. [13], Ce addition to 13 the Al-20Si alloy, resulted in an improvement in both ductility and tensile strength, due to a 14 decrease in the size and change in the morphology of the primary and eutectic Si crystals. Ce 15 addition refined the primary Si grains of an Al-17Si alloy and reduced the liquid temperature. 16 Maja vončina et al. [14] reported that Ce modifies the eutectic Si structure and induces a 17 transition from a coarse flake-like and acicular shape to a fine fibrous structure and discrete 18 particles with an increasing concentration. The addition of Ce improved the tensile strength and 19 ductility of the Al-Si alloys through modifying their microstructures. Gröbner et al. [15] 20 reported that the Ce phases serve as the nucleation sites for the aluminum or silicon crystals in 21 both the hypo and hypereutectic Al-Si alloys. However, Mehdi and Malakhov [16] found that 22 the addition of 0.03wt%–0.2wt% Ce neither modified the microstructure nor noticeably affected 23 the grain size of the Al-Si alloys. Ao et al. [17] investigated the effect Ce addition on the 24 microstructures and mechanical properties of the A380 aluminum alloy. It was reported that the 25 modification effect was no longer noticeable when the added Ce content was greater than 26 0.5wt% and the 0.3wt% Ce alloy depicted a high ultimate tensile strength and ductility.

The ternary Al-Si alloy is widely used in the automotive industry due to its increasing importance for bringing lightweight and high strength characteristics. The precipitation of the intermetallic phase and the solubility of ternary elements in the matrix are the two most crucial factors to take into account when choosing the ternary elements. Solid solubility strengthens existing phases while ensuring modification through changes in equilibrium rather than solute

1 buildup in the liquid [18]. The Al-Si-Cu alloy shows higher strength than binary Al-Si alloy and 2 their corrosion resistance is better than Al-Cu alloys. The addition of Cu to the Al-Si alloy 3 increases the wear resistance of the alloy by increasing the matrix solid solubility and the 4 formation of hard and brittle intermetallic Al<sub>2</sub>Cu phase [19]. According to Ceschini and Toschi 5 [20], the addition of modest amounts of Si, Cu, and Mg causes the precipitation of Al<sub>2</sub>Cu and 6 Mg<sub>2</sub>Si phases, which improves hardness and strength, and hence the wear resistance of Al alloys. 7 Dasgupta and Bose [21] concluded that the wear resistance of the Al-Si alloy increased with Cu 8 addition because of the Al<sub>2</sub>Cu phase. Another study [22], showed that the wear rate is not 9 appreciably affected by the addition of Cu. However, the addition of Cu increased the transition 10 load. The influence of the combined action of grain refiner and modifier on dry sliding wear of 11 the Al-12Si-3Cu alloy showed the best wear resistance at higher loads [23]. For a given Al-Si 12 alloy, the Si particle shape can be modified by using modifiers during the melting and casting 13 process and or heat treatment methods.

14 The impact of heat treatment for Al-Si base alloys containing Cu and/or Mg have been reported 15 [24]. Traditional solutionzing and ageing processes are employed to alter the morphology of Si 16 particles in Al-Si based alloys [25]. Hazra et al. [26] reported that the improvement in the wear 17 resistance at the higher temperature after heat treatment was attributed to the additional 18 strengthening from age hardening that occurred during the wear process. This improvement was 19 attributed to microstructural modification upon heat treatment. The enhancement in the wear 20 properties of Al-Si-Cu alloys after heat treatment has been mainly attributed to the formation of 21 non-equilibrium Al<sub>2</sub>Cu precipitates within the primary dendrites and changes in Si particle 22 morphology. The amount and coarsening of precipitation vary depending on the ageing 23 temperature and its duration. The addition of 0.05 wt. % Ce changed the morphology of the Al-24 Cu phase in an Al-Si cast alloy from crumbled to fully form [27]. In addition, Ce element reacts 25 with Si to form CeSi<sub>2</sub> which may promote the heterogeneous nucleation of the intermetallic 26 phase. However, excessive Ce will lead to the loss of Si content, which in turn reduces the 27 fraction of the main strengthening phase. Therefore, adding suitable Ce content will be an 28 effective method to modify the Al<sub>2</sub>Cu phase in Al-Si-Cu alloys [28].

However, investigations are lacking on the wear behavior of thermally aged and Cerium modified hypereutectic Al-Si alloy. In the present work, the influence of ageing time on the wear behavior of Ce modified (T6) and thermally aged Al-18Si-3Cu alloy was investigated and
 compared with the basic and modified alloys.

3

## 4 **2. Experimentation**

5 In the present work, an electrical resistance furnace was used to melt the base (Al-18Si-3.6Cu) 6 alloy at 850°C (Make: NANOTECH, Chennai, India; Power 3-6 kW; Material loading capacity, 7 1-10 kg). The melt temperature was continuously monitored with K-type thermocouples. The 8 base alloy of 3 kg was loaded into the preheated (500°C) crucible. The preheated Al-15wt% Ce 9 master alloy pieces were added into the melt and were then stirred for 25 min to ensure 10 composition homogeneity. To ensure a low hydrogen content, the melt was degassed with 6 g of 11 solid hexachloroethane (C<sub>2</sub>Cl<sub>6</sub>). Billets were prepared by pouring the molten metal into a metal 12 mold that had been preheated at 150°C. The chemical composition of as-cast alloys was 13 determined by X-ray fluorescence (XRF) using a Philips X-ray spectrometer (model PW 1480); 14 the findings are presented in Table 1. A report [17] states that once the additional Ce 15 concentration exceeded 0.5 wt%, the modification effect was no longer noticeable. Therefore, in 16 this study, 0.34 wt.% of Cerium was added to the base alloy. For the microstructural study, the 17 samples were ground, polished, and etched using a Keller etchant and examined through an 18 optical (ZYNAX) microscope and a field emission scanning electron microscope (Model: JEOL 19 JSM-6480LV) using secondary electron (SE) and Working Depth (WD) imaging modes, 20 whereas chemical compositions of the constituent phases are examined using an energy 21 dispersive X-ray (EDX) micro-analyzer attached to the SEM. The SEM is operated at an 22 acceleration voltage of 10-30 kV. The base, modified and age-hardened alloys were machined 23 into cylindrical pins of 30mm  $\times$   $\Phi$ 10 mm. The T6 heat treatment was carried out in a muffle 24 furnace. The alloy was solution treated at a temperature of 500 °C for 1 h and quenched to room 25 temperature followed by an aging treatment at 210 °C for 1hr, 3hr, 5hr and 7 hr.

26

#### Table 1. The chemical constitution of the Al-18Si-3.6Cu-0.34Ce alloy (Grade3XX.X)

| Elements | Si | Cu   | Ce   | Al      |
|----------|----|------|------|---------|
| Weight%  | 18 | 3.66 | 0.34 | Balance |

1 Brinell hardness (BH) test was conducted according to ASTM E10 using a 2.5 mm diameter ball 2 indenter (SAROJ, Optical Brinell Hardness Tester, B-3000). Readings of the microhardness of 3 the alloys were taken 20 times under a load of 62.5 kg. Wear tests of the unmodified, modified 4 and modified heat-treated samples were carried out on a Pin-on-Disc wear testing machine 5 [DUCOM WEAR & FRICTION MONITOR -TR-20LE) having a EN-32 steel disk. The loads 6 were varied at 10, 20, 30, and 40 N while the sliding velocity and sliding distance were kept to 7 1.0 m/s and 2000 m respectively. Figure 1 shows the wear testing set-up used in this 8 investigation.



9

10

Figure 1. Dry sliding Pin on Disc type wear testing machine

11

12 Volumetric wear rate and wear resistance were calculated by using equation (1) and equation (2)

$$V = \frac{\Delta m}{\rho} \tag{1}$$

Wear resistance = 
$$\rho/\Delta m$$
 (2)

Where  $\rho$  is the density and  $\Delta m$  (weight of a pin before test - weight of a pin after test) is the sliding wear measured as the weight loss of the samples using a high precision digital weighing scale (WENSAR, PGB-301, 0.01 mg accuracy). Interface temperature measurement at the pin during the sliding was carried out using a chromel-alumel thermocouple placed at 1.5 mm away from the sliding surface. Interface temperature and friction force were recorded after every 2 min of sliding time and the average values were reported. The ratio of the average frictional force to the normal force is known as the average coefficient of friction.

## 2 **3. Results and discussion**

## 3 *3.1. Microstructures*

4 Figure 2(a) shows the optical microstructure of the base alloy, which consisted of a block like the 5 polygonal form of primary Si with sharp edges, with random distribution of long acicular 6 eutectic Si phase and the distinctive reticular-shape of inter metallic phases and columnar grains 7 of α-Al matrix. The microstructure of the Al-18Si-3.4Cu-0.3Ce alloy (Figure 2b) shows reduced 8 size, rounded and more regular Si edges and angles, increased α-Al spheroidization, and uneven 9 distribution of the intermetallic phases at the interface between the eutectic Si and α-Al matrix. 10 The addition of Ce clearly transformed the large-acicular, plate-like eutectic Si into a fibrous and 11 dendrite Al phase into round branches with less interface separation. Figure 2(c-f) shows the 12 microstructures of the modified and T6 heat treated alloys at different aging times. As observed, 13 in the microstructure of 1hr and 3hr age-hardened alloys (Figure 2c,d) the spheroidization of 14 both primary Si of eutectic silicon phases and precipitation of fine intermetallic phases were 15 observed. The microstructure of the alloy after 5 hr of ageing revealed the formation and 16 homogenous distribution of coherent fine Al<sub>2</sub>Cu precipitates at the grain boundary as well as changes in the eutectic Si into fine and spherical particles. The microstructure of the modified 17 18 and 7 hr age-hardened alloy is shown in Figure 2(f). It is observed that after the age-hardening 19 process, there is no change in the shape of primary and eutectic Si. However, the coarse Al<sub>2</sub>Cu 20 phase with a branched network can be noticed in the 7 hr age-hardened alloy.



Figure 2. Optical microstructure of (a) base (b) modified (c) 1 hr age (d) 3 hr (e) 5 hr and (f) 7 hr age hardened alloy

2 3

4 SEM/EDS images of the base alloy (Figure 3) showed the presence of plate-like coarse primary 5 Si (light gray), eutectic needles/plate, and  $\theta$  (Al<sub>2</sub>Cu) intermetallic compounds (white contrast) 6 randomly scattered throughout the matrix. The EDS results of the phase composition of the cast 7 alloy is shown Table 2. Figure 4 shows the SEM /EDS microstructure of the modified alloy. It 8 was clearly observed that the addition of Ce significantly changed the morphology of the primary 9 Si, the eutectic phase and  $\alpha$ -Al grains. Improved alloys have the primary Si particles of spherical 10 form corners, refined eutectic Si, and significantly modified with globular α-Al matrix. It was 11 clear that the uneven distribution of  $\theta$  and Cerium rich (AlCe and Al-Si-Cu-Ce) intermetallic 12 phases at the interface between the eutectic Si and  $\alpha$ -Al matrix. The chemical analysis by EDS 13 studies of the Al-18%Si-3.6Cu-0.3%Ce alloy showed (Table 3) the presence of a Ce-rich phase

in the sidewall of the  $\theta$  phase, which could be described as Al<sub>2</sub>Ce-Si-Cu (Spectrum no-2). It can be clearly seen that Al<sub>2</sub>Cu contains higher Ce (the mass fraction of Ce is approximately 16.79%) and Al<sub>2</sub>Cu becomes coarser when Ce is added to the Al-Si-Cu alloy. It can be speculated that the variation of morphology is caused by the partial dissolving of Ce in Al<sub>2</sub>Cu. In the Ce-modified alloy, Al<sub>2</sub>Cu eutectic was more compact, with much smaller surface area compared to the base alloy.



7

8 9

Figure 3. SEM/EDS micrograph of the cast Al-18%Si-3.6Cu alloy

#### Table 2. The composition analysis of different phases of by EDS

| Spectrum position | Phase              | Al-K  | Si-K  | Fe-K | Си-К  |
|-------------------|--------------------|-------|-------|------|-------|
| pt1               | α-Matrix           | 94.44 | 0.80  | 0.00 | 3.94  |
| pt2               | Primary Si         | 0.00  | 100.0 | 0.00 |       |
| pt3               | Al <sub>2</sub> Cu | 44.8  | 0.98  | 0.34 | 53.56 |
| pt4               | Eutectic Si        | 45.72 | 50.13 | 0.89 | 1.57  |





 Table 3. The EDS result of phase composition of Ce modified alloy

| Spectrum position | Phase                    | Al-K  | Si-K  | Fe-K | Cu-K  | Ce-K  |
|-------------------|--------------------------|-------|-------|------|-------|-------|
| pt1               | Primary Si               | 0.94  | 98.90 | 0.00 | 0.16  | 0.00  |
| pt2               | Al <sub>2</sub> Ce-Si-Cu | 55.89 | 6.64  | 0.00 | 20.69 | 16.79 |
| pt3               | α-Matrix                 | 98.09 | 0.97  | 0.34 | 0.91  | 0.02  |
| pt4               | Eutectic Si              | 32.91 | 65.00 | 0.89 | 1.94  | 0.15  |
| Pt5               | Al <sub>2</sub> Cu       | 45.8  | 0.98  | 0.00 | 52.51 | 0.34  |

3 The SEM microstructures of the modified alloy after hardening for the 1hr, 3hr, 5 hr and7hr are 4 shown in Figure 5. The microstructure of 1hr age hardened (Figure 5a) alloy depicts the presence 5 of the primary Si and Si eutectic phases with rounded and fine precipitation of  $\theta$  and Ce rich 6 phases. The microstructure the modified and 5 hr age hardening (Figure 5c) alloy exhibited a 7 significant volume fraction of medium-sized Al<sub>2</sub>Cu intermetallic particles in the  $\alpha$ -Al matrix. It 8 can be seen by comparing Figure 5(b) and Figure 5(c) that the amount of fine Al<sub>2</sub>Cu precipitates 9 increased as the ageing period increases. However, the microstructure of the 7-hour aged alloy 10 (Figure 5d) revealed the presence a coarse  $\theta$  phase close to the Si phase. The increasing ageing 11 time, the solute atoms segregate from the supersaturated solid solution and become fine  $\theta$ 12 precipitates initially and causing agglomeration of the precipitating phase form a coarse  $\theta$  phase. 13 The precipitation sequence in the Al-Si-Cu alloy is influenced by the high density of dislocations 14 that form during quenching close to the Si-rich zone because of the high difference in thermal 15 expansion between the Si particles and the  $\alpha$ -Al matrix. As a result, the coarse phase develops on 16 the dislocations close to the Si particles.



Figure 5. SEM microstructures of the modified and age hardening alloys after: (a) 1 hr, (b) 3hr, (c) 5hr and (d) 7hr

2 3

4 The cast Al alloys contain pro-eutectic solution, eutectic mixtures of Al and Si and precipitated 5 particles. The solubility of Cu in the Al matrix increased owing to the high-temperature solution 6 heat treatment. The dissolved solutes remain in the solid solution during quenching at room 7 temperature. The microstructural evolution due to the aging treatment was mainly attributed to 8 the increased precipitation of  $\theta$  phase. Metastable precipitates with various structures 9 sequentially appear and disappear as the alloys are aged. The precipitation pattern of diluted Al-Cu alloys is a well-known example represented as SSS  $\rightarrow$  GP1  $\rightarrow$  GP2 (or  $\theta'') \rightarrow \theta' \rightarrow \theta$ . Where 10 11 SSS is the supersaturated solid solution after solution treatment and quenching. Nano-sized 12 coherent pre-precipitates (or solute clusters), called Guinier-Preston (GP) zones are formed 13 during natural aging and in the early stages of artificial aging. Here, GP1 and GP2 refer to the 14 solute-rich regions formed in the first and second stages of aging, whereas the  $\theta'$  and  $\theta$  are stable

1 phases characterized by coarse and fine particles that are typically observed in over aged and 2 optimum ageing conditions respectively [29]. At room temperature, Cu in the Al-Si alloy leads to 3 the formation of GP zones and with a further increase in the temperature to 100°C leads to the 4 dissolution of GP zones, forming a coherent  $\theta'$  phase with a double-layer structure consisting of Al 5 and Cu. Prolonged aging dissolves the GP zone and in homogeneously nucleates metastable 6 phases on dislocations. Owing to the difference in thermal expansion coefficients of the primary 7 Al and Si particles, low-energy and high-density dislocations form in Al-Si-Cu alloys. These 8 sites act as heterogeneous nucleation sites for the  $\theta'$  phase, forming a stable, incoherent ( $\theta$ )-9 Al<sub>2</sub>Cu phase) with aging, which increases the nucleation rate of the  $\theta$ -Al<sub>2</sub>Cu phase, suppressing 10 the growth of Al<sub>2</sub>Cu phase during aging, thereby increasing the volume fraction of the  $\theta$  phase 11 [30]. The fragmentations of Al, Al<sub>2</sub>Cu, and Si eutectic phases within the matrix are redistributed 12 during age-hardening. During the holding period, the dissolution of the Cu-rich phase raises the 13 concentration of Cu and Si in the matrix. Finally, prolonged ageing causes precipitated particles 14 to become coarse and incoherent with the Al matrix.

#### 15 3.2. Hardness

16 Figure 6 shows the results of hardness values of the base, modified and age-hardened alloys. The 17 hardness of the alloys with and without the Ce addition are 90 and 96 HB. The results indicated 18 that the Ce addition contributed to an improved hardness value than the base alloy, possibly due 19 to an increase in the fiber form of the eutectic Si phase. Furthermore, the age hardening treatment 20 increased the hardness and the 5hr age hardened alloy showed the highest hardness of 125 HB. 21 However, with a further increase in the ageing time, the 7hr age hardened alloy showed a lower 22 hardness value of 114 HB. The increase in hardness in the modified alloy could be owing to the 23 formation of nearly spherical primary Si and changed dendrite eutectic silicon into a fine fibrous 24 form and relatively hard Al<sub>2</sub>Cu and Al<sub>2</sub>CeSi phases in the refined Al matrix. Higher hardness 25 may be partially attributed to Ce dissolving in Al<sub>2</sub>Cu. The presence of the Ce-rich phase close to 26 the Al<sub>2</sub>Cu phase increased the hardness. The solid solubility of Cu in Al-matrix during the 27 solution treating process could also be attributed to an increase in the hardness of the alloy. The 28 precipitates of fine particles Al<sub>2</sub>Cu in the matrix and spherical eutectic Si phases obtained during 29 the age hardening reduced the stress concentration at the interface of Si particles and α-Al 30 matrix. As a result, the tendency to initiate subsurface cracks decreased, resulting in an increase 31 in hardness. With increasing ageing time, the solute atoms segregate from the super saturated

solid solution and become fine Al<sub>2</sub>Cu precipitates initially and gradually become coarse and
incoherent with the matrix. This makes it easy for the dislocations to penetrate the surface and
lowers the shear stress and thus, decreases the hardness [31].





5

Figure 6. Hardness of base, modified and modified with heat treated alloys

## 6 *3.3. Interface temperature*

7 The variation of interface temperature with the load is shown in Figure7 at a constant sliding 8 speed of 1.0 m/s. It is observed that the interface surface temperature increases linearly with the 9 increasing load. The base alloy shows a higher interface temperature than that in the modified 10 and heat-treated conditions. The alloys in age hardening condition do not affect the interface 11 temperature substantially; however, the interface surface temperature decreases with the 12 increasing age hardening time. It is observed that the 5hr age-hardened alloy exhibits low 13 interface surface temperature throughout the load range compared to the other age hardened 14 alloys. The amount of oxidation formation and thermal softening of the matrix depends on the 15 interface temperature, which influences the wear rate and friction force. The presence of coarse 16 primary Si particles with sharp edges and corners, needle-like eutectic phase and brittle 17 intermetallic phases in the base alloy are less cohesive with the matrix, which causes the matrix to soften easily and the high plastic flow of metal. This results in increasing the area of contact, 18

1 leading to a high friction force and a high interface temperature. The cast condition, Si and 2 intermetallic phases of the alloy act independently that may facilitate the yielding of asperities 3 and increasing the actual area of contact, hence, increase in the interface temperature. The 4 modified and heat-treated alloy has a high hardness and strength due to the modified Si particles, 5 fine precipitation of Al<sub>2</sub>Cu intermetallic, increased solid solubility, and greater cohesiveness with 6 the matrix, which resists asperity yielding and gross plastic deformation near the surface layer, 7 making the oxide protective film more stable and reducing the real area of contact resulting in 8 less interface temperature [32].



9

10 11

Figure 7. The variation of the interface temperatures with the load at a sliding velocity of 1.0m/s

#### 12 3.4. Wear behavior

Figure 8 depicts the variation in wear rates with loads at sliding velocity of 1.0 m/s. It has been noted that the wear rate increases as load increases, and as expected, the base alloy exhibits a higher wear rate than the modified alloy. The age-hardened modified alloys show a lower wear rate and 5 hr age hardened alloy exhibits the least wear rate as compared to the 1hr, 3hr and 7 hr age-hardened alloys. At the loads of 10, 20, 30, and 40 N, the 7hr age-hardened alloy exhibits approximately 17%, 57%, 70%, and 67%, higher wear rates respectively compared to the 5hr age hardened sample. Figure 9 depicts the relationship between the load and wear resistance (reciprocal of wear rate) of the basic, modified, and age hardened alloys. It has been found that the wear resistance diminishes with the increasing load and is greater at a low load of 10 N. The base alloy has lower wear resistance than the modified alloy, and as the age hardening time increases, the wear resistance rises. The 5hr age-hardened alloy, in contrast, shows the highest wear resistance over the entire load range, while the 7hr age-hardened alloy exhibits lower wear resistance.

8 Age hardening also increases the hardness due to increased area fraction of clusters of Al<sub>2</sub>Cu 9 phase along the interface of primary Si particles. The diffusion of the alloy increases the bonding 10 between Si and the Al-matrix resulting in a higher resistance of the matrix to plastic flow [33]. 11 Uniform distribution of fine and spheroidized Si crystals surrounded by fine precipitates of 12 Al<sub>2</sub>Cu would retard the nucleation and crack propagation and therefore, can be attributed to the high wear resistance of the 5hr age hardening alloy. As the aging time (7hr) increased, hardness 13 14 decreased because the precipitates transformed gradually from metastable state to a stable state, 15 and finally to an incoherent interface between the precipitates and matrix. According to Ostwald 16 ripening [30], the solute atoms get segregated from the supersaturated solid solution and coarsening of precipitates by dissolution of the smaller precipitations due to reduction of surface 17 18 energy. When the precipitates become large and few, the distance between the precipitates 19 increases, therefore surface becomes easier for the dislocations to pass through and resulting in a 20 decrease in shear stress and therefore decrease in the hardness and wear resistance.



Figure 8. The variation of wear rates with the loads at 1.0 m/s sliding velocity





Figure 9. Variation of wear resistance with the load at 1.0m/s sliding velocity.

1 The specific wear rates of the base, modified and aged alloys under different loads are shown in 2 Figure 10. In the present investigation, it was observed that the specific wear rate varied in a 3 range between  $10^{-04}$  to  $10^{-03}$  mm<sup>3</sup>/N-m. According to the values of the specific wear rates, the 4 state of wear was classified as mild wear ( $w_s=10^{-07}$  to  $10^{-04}$  mm<sup>3</sup>/N-m) caused by oxidative wear 5 and severe wear ( $w_s \ge 10^{-03}$  mm<sup>3</sup>/N-m) induced by adhesive and abrasive wear [34].





Figure 10. The variation of the specific wear rates with the load and sliding velocity of 1.0 m/s

8 It has been shown that the specific wear rate for basic alloys, modified alloys, and 7-hour aged 9 alloys increases in the low load range between 10N and 30N and further decreases at high loads 10 between 30N and 40N. The specific wear rates of the other age hardened alloys gradually 11 decreased with the aging times and the 5 hr age hardened alloy showed a low specific wear rate. 12 An increase in load results in an increased real contact area between the mating surfaces, which 13 gives rise to an increased wear rate. The high wear rate in the base alloy was attributed to the 14 penetration of the hard and coarse primary Si particles in the matrix. The modified alloy showed 15 a reduced wear rate owing to the presence of smooth edges, near-spherical morphology of Si and 16 eutectic silicon phases and refined grains of Al matrix. This would cause low stress 17 concentration at the particle-matrix interfaces and resist the crack nucleation and their growth. 18 Furthermore, the precipitation of fine intermetallic Al<sub>2</sub>Cu phase distributed in the inter-dendritic

1 regions may be attributed to the reduction in the wear rate [35]. The Al<sub>2</sub>Cu precipitates at the 2 grain boundaries of the primary Si phase strongly strengthen the matrix during ageing by 3 increasing the bonding between the spherical Si, the second phase particles, and the matrix, 4 resulting in greater resistance to plastic flow [36]. On the other hand, increased ageing time 5 increases the diffusion rate and precipitation of high volume of the hard Al<sub>2</sub>Cu phase, resulting in 6 an increase in hardness [37]. The presence of near-spherical morphology of hard primary Si and 7 eutectic silicon phases, Al<sub>2</sub>Cu and Al<sub>2</sub>CeSi intermetallic phases in the soft Al matrix can enhance 8 hardness and give better wear resistance. The strengthening of alloys by the formation of fine 9 precipitates that is highly coherent with the matrix. Once the coarsening of the precipitates 10 occurs, they cannot be coherent with the matrix again. Kaçar et al. [38] indicated that in the over-11 aged (7 hr) condition, the precipitates were relatively large, and this significantly reduced the 12 hardness and wear resistance.

## 19 3.5. Co-efficient of friction ( $\mu$ )

20 The variation of the average coefficient of friction with the load is shown in Figure 11. The 21 coefficient of friction was found to be low at 10N and increased with increasing the load. The µ 22 values of the modified alloy had a lower coefficient of friction than the base alloy, and the age 23 hardened alloy revealed a lower coefficient of friction and a declining trend with increasing 24 aging time. In addition, it was observed that the 5hr aged alloy had the lowest coefficient of 25 friction compared to the other alloys. The alloy aged for 5h causes spheroidization of Si phase 26 and increases the volume fraction of hard Al<sub>2</sub>Cu particles. These changes in the microstructure of 27 5 hr age-hardened alloy relieve the stress concentration at the interface of the Si/Al and therefore, 28 can effectively suppress crack propagation at the spheroidized Si and Al interface. Thus, 29 reducing fracture and deformation of the surface asperities results in a low coefficient of friction. 30 This reduction in the coefficient of friction may attribute to the fact that higher amount of 31 precipitates and higher hardness of the aged alloys may reduce the real contact area.



Figure 11. The variation of the average coefficient of friction with the load at a sliding velocity of
 1.0 m/s

## 4 3.6. Worn surface morphology and wear map

5 Figure12 displays the worn surfaces of the base, modified, and age-hardened alloys after sliding 6 for 2000 m at 40 N load and 1.0 m/s sliding velocity. It was observed in the worn surface of the 7 base alloy (Figure 12a) exhibited marks of severe damage, the higher degree of deep grooves, 8 scratches, furrows, and the delamination surface with large cavities. Cracks in the vertical 9 direction of the wear track, and spalling on both sides of the wear track, indicated adhesive wear. 10 At a higher load of 40 N, the softening of the surface took place due to the frictional resistance 11 resulting from the surface material of the alloy getting welded to the counter face surface. Due to 12 the increase in adhesive nature of the pin and the alloy, delamination occurs easily. The worn 13 surface of the modified alloy is shown in Figure 12(b). It was observed that the extent of 14 delamination appeared to be less compared to that of the base alloy. The depth of valleys and the 15 width of grooves were found notably less, and the undulations observed on the worn surface 16 were considerably less. Figure 12(c-e) depicted the worn surface of modified and age-hardened 17 alloys. As a result of mild wear, it had a reasonably smooth surface with fine abrasion grooves. 18 The worn surface also had a tiny number of small dimples and only a few scoring marks

stretching from one end to the other. The worn surface of the modified 5 hr age hardened alloy 1 2 (Figure 12d) revealed a smooth surface, with fine scoring and uniform wide grooves. It is also observed that white areas on the surface are indicative of oxide formation. 3





Figure 12. SEM worn surfaces at the load of 40N and sliding velocity of 1.0 m/s for(a) base (b) modified, (c) 1hr aged, (d) 3hr aged, (e) 5hr aged and (f) 7hr aged alloys.

1 Figure 13 shows different wear regimes as a function of the loads. The wear map was 2 constructed based on wear rate values and the worn-out surface morphologies. Low to moderate 3 wear was controlled by oxidation wear, while mild wear was primarily controlled by oxidation 4 and the abrasive mode of wear. Severe wear was prominently controlled by plastic deformation 5 (adhesive wear) and abrasive wear. It was observed from the figure that the base alloy showed 6 mild wear at loads up to 30 N and beyond, and the wear mechanisms of the base alloy could be 7 defined by both oxidative and abrasive wear. At a higher load closer to 40 N, the wear in the 8 base alloy was severe (plastic deformation induced), and the wear mechanism was controlled by 9 both adhesive and abrasive mechanisms. In the modified alloy, up to a load just beyond 10 N, 10 there existed low mild wear (purely oxidative), a larger mild wear regime, and a transition from 11 mild wear to severe wear closer to 40N load. The severe wear regime was smaller in the 12 modified alloy as compared to the base alloy. This could be due to the modification of Si, 13 eutectic Si, and intermetallic phases. A comparison of wear among the age-hardened alloys showed the largest severe wear regime in the 7-hr age-hardened alloy, whereas the 5 hr age-14 15 hardened alloy showed very minimal severe wear. Because of the high hardness and abundance 16 of small Al<sub>2</sub>Cu precipitates, alloys that have been age-hardened for five hours may not experience as much severe wear. At higher load, the wear mode combines a little oxidative, more 17 18 adhesive, and abrasive forces. However, the Ce-modified alloy with 5-hr age hardening produced 19 the best wear behavior at all loads between 10 and 40 N.



Figure13. The wear mechanism map at different loads and 1.0 m/s sliding velocity.

## 2 **4.** Conclusion

3 The effects of microstructural modification by Ce addition and post-heat treatment by age 4 hardening at various ageing periods on the wear properties of an Al-15Si-3.6Cu alloy were 5 investigated and the following conclusions can be drawn.

6 1. The cerium modified alloy microstructure demonstrated a significant change in the primary Si 7 coarse sharp edges, long needle/acicular eutectic phases, and intermetallic phases into spherical 8 and globular eutectic Si and intermetallic particles. The microstructure of the modified and age 9 hardened alloy revealed precipitation of fine Al<sub>2</sub>Cu and further refining of eutectic Si and Al-Si-10 Ce phases.

Increasing ageing time increased the amount of precipitated particle at the grain boundary,
 which hindered the dislocation movement. With the further increase in the ageing time, the
 precipitated participles became coarse and incoherent with the matrix. The coarse particles
 allowed the dislocations to move freely.

15 3. The hardness of the modified alloy was higher than the base alloy. The modified and age16 hardened alloy reached the maximum hardness at 5 hr age hardening condition.

4. The wear properties of Al-15Si-3.6Cu alloy are considerably improved by the addition of the
Ce modifier and age hardening. The wear rates of modified and age-hardened alloys increased
with an increase in the ageing time and the 5 hr age-hardened alloy showed the lowest wear
under the loads ranging from 10 to 40N.

5. The interfacial temperature and friction coefficient of the modified and age-hardened alloys
were less than the base alloy. The 5 hr age-hardened alloy exhibited the lowest coefficient of
friction in the entire load range, which indicated a higher wear resistance.

6. All modified and age-hardened alloys showed a transition from lower mild to mild and to
severe wear mechanisms but the 5hr age-hardened alloy displayed very little sever wear and
smallest mild wear zones for the selected loading conditions.

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