Effects of New Modification and Refinement Techniques of Mechanical Properties and Corrosion Behaviours of Al-Si Alloys

Hussein. A. Hussein, Mohammed. j. kahdim, Alaa. A. Atiyah

1Department of Production Engineering and Metallurgy / University of Technology, Baghdad – Iraq.
2Department of Materials Engineering / University of Technology, Baghdad – Iraq.
*Corresponding author: 70082@uotechnology.edu.iq

Abstract. In this paper, the effects of new techniques of phosphor-doped elements on the microstructure and mechanical properties of Al-18Si alloy to produce modifier compounds were studied. The modifiers were produced by developing a new technique and additions field (nano-doped metals) under as-cast conditions. The results show that the addition of CuPO₄, Ni₃(PO₄)₂ and Ca₃(PO₄)₂ to the Al-Si alloys can change (refine) the primary Si phases and are less angular. In addition, the eutectic Si form has changed from a long needle-like to a fibrous shape. The modified Al-Si alloys have microstructures in the inter-dendrite region consisting of a uniformly distributed α-Al phase, eutectic Al-Si, and fine primary Si particles. The microstructure showed that the primary silicon fraction decreased 60% with increased phosphorus elements content. The finest microstructure could be observed with a 0.03% addition of doped metals. Good enhancements in ultimate tensile strength and elongation with clear increases in the hardness were observed, reaching 55%, 9% and 30%, respectively. Moreover, additions give the possibility of changing corrosion behaviours from pitting corrosion to micro and general corrosion. Furthermore, the optimal holding and melting temperature is 780°C, with a holding time of 15 minutes.

Keywords: Aluminium Silicon, Corrosion Resistance, Wear Resistance, Fracture Behaviour.

1- Introduction
The Al-Si eutectic and primary Si alteration in hypoeutectic alloys play a significant role in developing mechanical properties and corrosion behaviours [1][2]. Grain size and morphology are the key microstructural factors that affect the processing and properties of alloys. A fine grain size leads, in general, to a decreased tendency to hot tearing [3], a more dispersed and refined porosity distribution [4] and improved directional feeding characteristics [5], although it can also reduce fluidity and cause defects in hot spots [5].

The improvement in the mechanical properties is believed to be due to the change in the size and morphology of eutectic silicon. It is well established that nucleation and growth during solidification play key roles in modification [6]. However, the detailed nucleation mechanism is still not well understood. Nucleation is difficult to study because of the complex role of the inherent impurities present in Al alloys. The novel entrained droplet technique first used by Zarif et al. [7] found that, unlike P, Sr refused to promote nucleation. However, the eutectic nucleation temperature is lowered by the contribution of Sr, which may be due to the formation of the intermetallic Al₆Si₅Sr layer, which may absorb or adversely affect the effective AlP nucleation sites. Min Zuo et al. [8] showed that the new Al-6Y-2P master alloy with cubic YP particles can also successfully develop complex modification properties for an Al-18Si alloy. By adding the intermediate alloy Al-6Y-2P, excellent dynamic changes of the Al-18Si alloy can be achieved. Under design conditions (780°C melting point, 1.5% additional melting point and 30–60 minutes holding time), the tensile strength and Brinell hardness of Al-18Si alloy can be significantly improved. It is proposed that the silicon atoms in the melt can improve the structural evolution of YP to AlP by releasing Y, which will lay the foundation...
for the excellent performance of a t composite modification. **Hongseok Choi et al.** [9] conducted experiments to study how nano-particles affect Si particles during solidification in hyper-eutectic Al–Si–Cu alloys. For instance, 0.5% c-Al$_2$O$_3$ nanoparticles are added and further dispersed using an ultrasonic cavitation technique. Microstructural analysis with optical and scanning electron microscopy revealed significant refinement of the central and eutectic Si particles as well. The primary Si particles were simplified from star shapes to polygonal or blocky shapes, and their edges and corners were much smoother. The study reveals that c-nanoparticles simultaneously refine and alter Si particles as well as decrease porosity in Al–20Si–4.5Cu. **Jiehua Li et al.** [10] studied the role of traces of phosphorus on nucleation in high purity Al-Si alloys. They proposed that only 0.25–2 ppm phosphorus is sufficient to form AlP. **Brian Cantor et al.** [11] reported the poisoning effect of sodium on AlP, concluding that the formation of Na$_3$P might reduce the amount of AlP, thereby increasing the eutectic silicon nucleation and growth temperature, i.e. higher undercooling (∆T). **S. Liang et al.** [12] confirmed this finding, noting that the ppm addition of sodium increased the eutectic droplet nucleation undercooling (∆T). The AlP is believed to be the potent nucleation site for eutectic silicon[11]. A recent publication [14] proposed that the addition of strontium caused the formation of intermetallic Al$_3$Si$_2$Sr. These intermetallic compounds may consume the AlP phase, thereby reducing the number of nucleated eutectic grains [13].

From this moment, grain refinement research focused on determining the key issues of core particles and the role of alloy composition, and many attempts have been made to integrate these two factors into the grain refinement model. Research in the age of twin planes usually emphasises one effect, and another effect sometimes leads to the proposition of various theories, but it is now obvious that, if these two factors (and the effect of processing conditions) are taken into account at the same time, a comprehensive grain refining model can be developed to correctly describe the grain-formation process.

This paper initially introduces recent theoretical developments in grain refinement that incorporate both nucleant particles and solute, after which the details of the role of solute and of inoculants are discussed. The main objective of this paper is to investigate in detail the effect of different levels of (Nano-doped metals) on primary Si and eutectic Si nucleation, as well as the mechanical properties and corrosion behaviour in the Al-Si alloy. Moreover, the phase’s reconstruction and phase structure are studied to illustrate the mechanism of intermetallic segments at some stage in the solidification process of the Al-Si alloy.

### 2. Experimental Method

#### 2.1 Preparation of Nano-dopant elements

One means of synthesising nanoparticles is by use of solid liquid chemical reactions in several steps. Step one: add metals powder (µm-in-size) and mix with 10ml of phosphoric-acid (H$_3$PO$_4$) for 72h at room temperature. Table 1 shows the chemical formula of the phosphoric acid and elemental powder chemical reactions. The reaction will continue until stopping. Step two is another reaction followed by 130°C for 12h. Step three is calcination at 720°C for 2h. Step four is grinding and evaluation by X-ray diffraction (phases and grain size).

| Material | Formulas |
|----------|----------|
| Cu       | 2 Cu + 2 H$_3$PO$_4$ = 2 CuPO$_4$ + 3 H$_2$ |
| Ni       | 3Ni + 2H$_3$PO$_4$ = Ni$_3$(PO$_4$)$_2$ + 3H$_2$ |
| CaO      | 3 CaO + 2 H$_3$PO$_4$ = Ca$_3$(PO$_4$)$_2$ + 3 H$_2$O |

#### 2.2 Master alloy preparation

The pelleted form of a master alloy consisting of 0.3g, and grain size is 300µm pure aluminium powder mixed with Nano-Metal-Phosphate and compaction powders below 150 bars to improve
oxidation resistance and flotation. Table 2 defines the elasticity of particles that have compressed together (nanoparticles and aluminium powder), and the pressure action leads to the contact points being fully bonded. Compact powder results in pellets which make handling easy.

### Table 2 The composition of pellets.

| Material       | Wt.% added | Wt.% added | Al-Pure | Compact pressure |
|----------------|------------|------------|---------|------------------|
| CuPO₄         | 0.01 g     | 0.03 g     | 0.3 g   | 150 bar          |
| Ni₃(PO₄)₂     | 0.01 g     | 0.03 g     | 0.3 g   | 150 bar          |
| Ca₃(PO₄)₂     | 0.01 g     | 0.03 g     | 0.3 g   | 150 bar          |

2.3 Casting techniques

The Al-13Si alloy was developed by liquid metallurgy. The chemical composition of the aluminium-silicon alloy used in this analysis is shown in Table 3. In the electric furnace (Carbolite, England), the alloy Al-13Si is heated to 780°C. Then, using an inert gas (Argon), degassing follows mechanical agitation with 500 rpm, as shown in Figure 1(a,b). At this point, the dopant-elements that were preheated to 350°C to eliminate any moisture content are added to the molten alloy. Particle-sized nano-metals (20 nm) were added (0.01and 0.03 %) to the molten alloy. The molten agitation was continued for about ten minutes to promote uniform dispersion of the wetting nuclant and uniform dispersion of the reinforcement. Then, the molten alloy was poured into the 1.5 cm x 15 cm preheated steel mould.

### Table 3 Al-Si alloy chemical composition (wt. %) used in this study.

|          | Bal. | Zn   | Ni   | Mg  | Mn  | Cu  | Fe  | Si   |
|----------|------|------|------|-----|-----|-----|-----|------|
| Al       | 0.004| 0.008| 0.02 | 0.01| 0.01| 0.14| 12.86|

2.4. Microstructural Analysis

Al-13Si alloy SEM photos were prepared by grinding via 220, 320, 600, 800, 1,000 and 1,200 grit sheets, respectively. The specimens were then polished with diamond paste (0.1µm), and the killer solution washed and etched. Keller’s reagent is a mixture of 5ml NHO₃, 3ml HCl, and 2ml HF, and 190ml H₂O, the solution used for microstructure detection.

2.5. Hardness Test

Vickers hardness tests were performed on the Al-13Si alloy (type ZWICK Z323 – Germany). For (10 seconds), the load was (0.5Kg). For each sample, three readings were used to obtain the average diameter value:
\[ H_V = 1.8544 \times \frac{P}{(D_{AV})^2} \]  
\[ \text{where} 
H_V: \text{Vickers hardness number}, 
P: \text{applied load (N)}, 
D_{AV}: \text{diagonal length (mm)} \]

2.6. Analysis of X-Ray Diffractions

The phases present in the alloy samples of modified Al-13Si were examined using X-ray diffraction via a Shimadzu X-ray diffractometer (XRD-6000) available at the Nano Technology Center University of Technology. X-ray tube: Cu, NF (1.54060 nm), radius of scanning: 185 mm, X-rays leakage: less than 2.5μSv / h at maximum output.

2.7 Corrosion Tests

The Al-Si alloy electrochemical analysis was concluded with cyclic polarisation. A computer-controlled device (PCI4/750, GAMRY, Inc., Warminster, PA) disbursed all tests in 3.5 % NaCl sol. In 25C. Ag / AgCl as the pole of reference and the auxiliary pole and working pole of noble metal (Pt) was used as the specimen keeper. The specimen was exposed to NaCl solution of 3.5 %. The area of exposure was 1 mm². Before each test, the samples were given a metallographic polish. Specimens were dipped into the solution until a steady open circuit (OCP) potential was obtained. The test specimens had an exposed area of about 10 mm². All data were neutralised by area of the surface and calculated using the Echem analyser to identify the test results evenly [15].

2.8. Wear rate measurement

Dry slip wear tests with ASTM F732-82 were conducted at room temperature using a laboratory pin on the disc wear test [11]. Nails, modified in Al-Si alloy o 10 mm and 20 mm in length, were polished with different sheets of grain carbide (220, 320, 500, 800, and 1,000) and cleaned with acetone and then dried. The wear device consists of a motor with a constant speed of rotation (510 rpm). The disk is made from tool steel with a 65 HRC hardness. Relative mass changes were tested by weighing the samples before and after wear using a sensitive-scale classification digital scale (DENVER Tool, Japan) (Max-210gm) of 0.0001 mg. The loads applied were 500 kN. After each test, the disk was cleaned.

The following equation was to calculate wear rate:

\[ \text{Wear rate} = \frac{\Delta W}{S} \]  
\[ S = V \times t \]  
\[ V = \frac{\pi DN}{1000 \times 60} \]

where

D: diameter (m) =0.14, W: The different in weight of sample before and after the test (gm), S: sliding distance (m), t: time (Sec), N: r.p.m=510, V: velocity (m/sec)

2.9. Tensile tests

Tensile tests on Al-Si alloy modifier specimens were performed with the dimensions shown in Fig. 2 (ASTM E8M) using Instron type 1195 machine made in England.

![Figure 2. Geometry and Standard dimensions of test specimen](image)
3. Results and Discussion

3.1 Microstructure of Experimental Materials

Fig. 3 illustrates unmodified Al-13Si alloy microstructures, initially composed by using J-Picture software of large grains of primary Si and platelet eutectic Silicon with a grain size equal to 37.32 µm.

![Figure 3. Microstructures of unmodified Al-13Si alloy.](image)

Fig 4(a) shows the morphology of Al-13Si alloys with 0.01% Ca₃(PO₄)₂ which consists of coarse-primary-Si-particles. Fig 4 (b) shows the morphology of Al-13Si alloys with 0.01 % Ca₃(PO₄)₂ which consists of coarse-primary Si particles of 1.71 µm in size with a fine eutectic Si distribution. When the Al-13 % Si base alloy contains 0.03 % Ca₃(PO₄)₂, the primary Si particles of 1.54 µm in size are scattered in an eutectic configuration of fibres leading to substantial refinement.

The Al₂Ca phase and primary Si formed in intimate association with each other as well as in association with the oxide inclusions. Previous experimental evidence suggests that Si particles may nucleate and grow on oxide biofilms during solidification of hypereutectic Al-Si alloys [14]. The primary Si nucleation on oxide biofilms may be attributed to the oxide film, which provides a powerful substratum for primary Si heterogeneous nucleation. Potential alignment and related misfits of the measured lattice between Si and AlP, Al₂Ca and the appropriate oxides. The misfit between Si and AlP is very close to zero, resulting in an incredibly strong potential for Si nucleation by AlP. The misfits between Si and the two popular Al₂O₃ types are too large for Si to serve as heterogeneous nucleants for the oxides. Al₂O₃ nanoparticles can be used in hypereutectic Al-Si alloy melts for simultaneous refining and alteration of Si[15].

![Figure 4. SEM microstructures of Al-13Si after additive Ca₃(PO₄)₂ (a) 0.01%, (b) 0.03%](image)
Fig. 5 (a, b) shows the microstructure of Al-13%Si alloy with different content: 0.01% NiPO₄ master alloy addition; primary Si size has decreased while the most of the eutectic Si became 3.28 μm. In increasing the amount of NiPO₄ to 0.03%, the primary Si size decreases to 2.67 μm. Fig. 4 (a, b) shows the distribution and size of primary Si; meanwhile, the eutectic Si is modified to short rod or dot shapes. However, both of the primary and eutectic Si become fine during accretion of the amount of NiPO₄ master alloy.

The hypereutectic alloys with primary silicon crystals are modified by AlPO, and the silicon crystals will otherwise be detrimental to the mechanical properties. The modification of the primary silicon crystals with AlPO reduces the size. The intermetallic phases are well distributed, found in the vicinity of the aluminium dendrites and in the aluminium-silicon eutectic [8]. The size of the primary silicon crystals was decreased by ~73% in the Al-13Si.

Figure 5 shows the microstructure of Al-13Si after additive Ni₃(PO₄)₂ (a) 0.01%, (b) 0.03%.

According to reaction equation, the AlNi intermetallic phase has a fibrous morphology, and the eutectic region consisted of Al₃Ni fibres and α-aluminium around the fibres per SEM micrographs of eutectic Si structures. These intermetallic compounds retard the grain growth, leading to grain refinement, and resulting in further strengthening effects[16].

Fig. 6 shows a microstructural examination, revealing the polygonal primary silicon particles, with an increasing addition of (0.03%) CuP distributed uniformly in the matrix. This could be due to the fact of reactions with the liquid Al forms AlP, Al₂O₃ and Cu₃Al particles present in molten alloy, which may act as heterogeneous nucleating sites for the modification of primary silicon particles and refinement of eutectic silicon during solidification of hypereutectic alloys [17]. Rich phases (intermetallics) Al₃Cu found partially dissolved in the dendrite matrix. After the main Al-Si eutectic reaction, intermetallics will be solidified in one massive and one fine eutectic form. The primary Si particle size increased with the addition of CuP (0.01 and 0.03%), ranging from 4.52–3.74μm, respectively, which is about a 60% reduction in primary silicon size.
3.2 Mechanical Properties

The results concerning mechanical characteristics show improved or comparable properties with the content of experimental material Nano-doped metals forms (Fig. 7). Vickers hardness is Hv=89.36 for the first sample without an additive. Vickers hardness are Hv=118.15 and 148.78, respectively in specimens with a content of 0.01–0.03% of Nano-copper-metals; moreover, Vickers hardness is Hv=102.24 and 120.71 respectively for specimens containing 0.01–0.03% of nano-nickel metals. The Vickers durability is Hv=95.64 and 114.71 for specimens with a content of 0.01–0.03% of nano-calcium metals. The difference in hardness is small, because the nano-doped metals are substituted, which means that the Al-matrix (fineness of each material) is very similar.

3.3 X-ray diffraction and crystallographic texture

The XRD pattern of Al-Si samples processed by a (Ca₃(PO₄)₂) master alloy is illustrated in Fig. 4.55. In order to investigate the extant form of Ca and its influence on the microstructure of aluminium alloy, Al-13Si samples are processed by Ca₃(PO₄)₂ and its phase composition analysis is shown in Fig 8 (a). It can be found that this alloy is composed of four phases, including α-Al, AlP, and Al₂O₃ primary Si. Al₂O₃ was observed through reflections on 2θ=12.19°, 21.17°, 38.54° and 47.86° and AlP was observed through reflections on 2θ=28.64° and 56.31° and Al₂Ca 19.15° and 44.95°. X-ray diffraction analysis shows the presence of Ca₃(PO₄)₂ in the synthesised sample as evidenced from reflections of low intensity [18]. The master alloy is composed of three elements: Ca, P and O. In this system, the atomic ratio of Al and P is about 1:1, indicating that all of the Ca atoms would react with Al to form Al₂Ca the atomic ratio of Al and Ca is about 2:1 without P. In comparison, from the phase
two alloys, it can be deduced that, with the addition of Ca₃(PO₄)₂, the Al-Si alloy appears [19]. The XRD diffraction pattern of the Al-Si alloy processed by NiPO₄ master alloy is illustrated in Fig. 4.59, showing the results of synthesis reactions using NiPO₄ master alloy. In order to investigate the extent form of Ni and AlPO and its influence on the microstructure of aluminium alloy, Al-13Si samples processed by NiPO₄ and the phase analysis are shown in Fig 8(b). This alloy is composed of four phases: α-Al, AlPO, primary Si and AlNi. AlNi was observed through reflections on 2θ=18.74°, 47.57°, 78.67° and 88.42° and AlP was observed through reflections on 2θ=47.54° and 69.24°. X-ray diffraction analysis shows the presence of NiPO₄ in the synthesised sample as evidenced from reflections of low intensity [20]. The master alloy is composed of three elements: Ni, P and O. The XRD pattern of Al-Si, indicating effective NiPO₄ is much more reactive and is thus a very suitable source for AlPO. Fig 8(b) shows that the formation of AlPO is induced and appears as a single-phase of high crystallinity according to the strong signals in the XRD pattern reveal the presence of trigonal (rhombohedral axes) AlPO and cubic AlNi. The phase fractions are analysed using calibration standards card.

The XRD diffraction pattern of the Al-Si alloy is processed by a CuPO₄ master alloy, as illustrated in Fig. 8(c). The microstructure was verified by means of X-ray diffraction (XRD). Apart from the obvious presence of aluminium, the diffraction pattern showed the presence of the Al₃Cu phase, as expected [21]. Subsequently, this method was chosen to characterise the microstructural evolution of the samples, since it allows the phase formation and dissolution to be correlated directly to the applied casting process. The introduced modification of the phase also permits the 2θ=20.70° to 78.31° region to be explored in the XRD pattern. It should be noted that the AlP and Al₂O₃ precipitates can be detected by the XRD approach, even if the small volume-fraction and small size of these precipitates are embedded in the Al matrix [22].

The XRD patterns from the extracted particles, as shown in 4.60, reveal the presence of cubic AlP, orthorhombic Al₂O₃ and cubic Al₃Cu in the sample. The phase fractions have been analysed using a calibration standards card.

Even after significant refinement and modification of the α-Al grain structure using intensive melt shearing, Al₃Cu was still the dominant phase. The XRD analysis further confirms that formation of AlP, Al₂O₃ and Al₃Cu, promoted by the addition of CuPO₄ grain refiner. Overall, the present results confirm that the production of intermetallic phase is primarily governed by the addition of a CuPO₄ grain refiner in Al-Si melts [23].
The relationships between addition nano-metal-phosphate and wear rate of experiments alloys are presented in Fig. 9. It is clear the wear rate decreases with an increase in percentage of nano-doped metal particles. Furthermore, the relationship is linear. Hence, a decrease in grain size and good distribution of primary Si, eutectic and intermetallic phases signifies a wear rate decrease regardless of the reinforcement nano-Al$_2$O$_3$ size and percentage. Also, the wear and tear rate of processed composites decreases with increasing modifier elements (nano-metal-phosphate). The improved wear resistance to a casting procedure is referred to the distribution of particles within the base Al and refinement of grain.
Figure 9. The variation of wear rate with sliding time with different nano-metal phosphates.

Figure 10. Optical micrographs of worn track: (a) as cast, (b) additive of (Ca$_3$(PO$_4$)$_2$) (c) additive of CuPO$_4$ (d) additive of Ni$_3$(PO$_4$)$_2$.

Fig. 10 shows an optical micrograph of worn surfaces of stir-processed composites. The micrograph reveals that the worn track breadth decreases in modified alloys compared to unmodified alloys. It is proof that the extent of wear and tear in a composite is below that of an unmodified alloy. The depth and breadth of the grooves generally imply an association in foster quantity of fabric from the specimen surface [26]. It is expected that uniform distribution of particles and modification of Si grains can cause a high wear resistance. Furthermore, the yield strength of the Al-13Si alloy is increased, which results in the strength of wear surface and the starting abrasive wear. Moreover, since Si is a hard material, it may plough out from the Al$_2$O$_3$ as the counter is slid across the face of the disc. In addition, the hard Si improves the resistance of a composite against plastic deformation and material flow by increasing the load-bearing capacity. The probability of adhesive wear is less in such Al$_2$O$_3$, and the dominant mechanism is abrasion and de-lamination.
3.5 Corrosion Behaviour

The cyclic polarisation curve was determined and shown in Fig. 11 to evaluate the electrochemical stability of prepared samples in 3.5% NaCl; corrosion variations were evident in the alloys tested. Cyclic polarisation experiments have been carried out in order to assess the polarisation domains for the analysed samples. All three possible domains – catholic domain, passive domain and transpassive domain – were shown by cyclic polarisation curves. The large passive dominance and low-density values show higher resistance to corrosion in the analysed sample in the transpassive domain [24].

![Figure 11. Cyclic polarisation curves of the experimental materials in 3.5% NaCl solution. (a) as cast, (b) additive of (Ca₃(PO₄)₂) (c) additive of Ni₃(PO₄)₂ (d) additive of CuPO₄.](image)

Indeed, despite the use of the Tafel extrapolation method for the determination of corrosion rates for Al-based alloys, the Tafel tables and their respective calculated uniform and pitting corrosion rates for metal covered with a semi-conductive passive film raised strong conviction [25]. Active dissolution near E_corr occurred in the polarisation curve of pure Al, followed by a major improvement of the current, with the potential added due to dilution and weakening of the passive layer, due to the attacks by Cl-anions shown in Fig. 12(a). The cyclic curves of polarisation also demonstrate the action of the board. This is obvious for the divisions of E_corr Al with the inclusion of phosphate elements, which displayed a certain curvature over the entire range of applications.

![Figure 12. Microstructure characteristics of the tested alloys after corrosion test. (a) as cast; (b) additive of (Ca₃(PO₄)₂) (c) additive of CuPO₄ (d) additive of Ni₃(PO₄)₂.](image)

As a result of microgalvanic corrosion processes, the effect of (Ca₃(PO₄)₂) on the micro pitting of alloys starts on the interface between the α-Al matrix. General irregular corrosion affected specimens,
with grey corrosion products covering their surface. The anodic current densities were almost unchanged, and the passive scale decreased by Ca$_3$(PO$_4$)$_2$ to 0.03%. With both changes, the curves displayed the same noble change in corrosion ability, the strong passive range and the same anodic current intensity. Al-13Si alloys revealed reverse and close hysteresis, indicating that these alloys are sensitive to micro-galvanic and micro-pitting characteristics of the tested Al-13Si alloys, per Fig. 12(b).

Fig.12 (c) shows the microstructure of Al-13Si alloys processed by CuPO$_4$ after a polarisation test in 3.5% NaCl. The Al-13Si alloys possess a typical structure of dendrite. The surface corrosion of all specimens indicates that Cl ions severely attacked the surfaces of the alloys during polarisation. The major type of corrosion is mico-galvanic and localised corrosion. While nano-galvanic corrosion occurred at the junctions of dendrites, corrosion appeared at both the junctions of dendrites and the interfaces of Al$_2$Cu and matrix. Furthermore, considering the initiation and growth of pitting corrosion [26], the corrosion type at a lower potential is general corrosion, while localised and pitting corrosion dominate at higher potentials, especially in a transpassive region.

The resistance of IGC is referred to the refinement of and enhanced creation of the precipitates in the matrix by 0.03 %NiPO$_4$, where increased precipitation in the grain boundaries is consumed their solute material, thereby reducing the compositional disparity between the matrix and the grain boundary area, by a modifier and discrete platelets in the grain borders [27]. Fig. 12(d) shows that the pitting susceptibility in NiPO$_4$ can be correlated with the modification of AlPO and AlNi-phase precipitates in grain bodies as well as in grain-boundaries, resulting in a finer and regular distribution of noble cathodes on the surface, as compared to the prevalence of grain boundary precipitation obtained in the 0.03% NiPO$_4$ sample variants displaying IGC susceptibility.

### 3.6 Fracture Analysis

A cross-sectional view of the fracture surfaces shown in Fig. 13(a) may further explain the failure mechanism. As a cast material, the crack extends along the crossroads between the centre and the limit of the softer areas, which was consistent along the surfaces of the fracture. With the de-cohesion of the Si particles, the voids coalesced and spread until a complete separation occurred and the sample failed under tensile loading. With a 0.01 percent of Ca(PO$_4$)$_2$, Fig. 13(b) shows the results of eutectic Si being changed, acicular with only tiny regions of a modified fibrous Si current, increasing the concentration of Ca(PO$_4$)$_2$ to 0.03%. In addition, the Si morphology transition revealed that intermetallic particles were found with the introduction of 0.03% of Ca(PO$_4$)$_2$. These particles have a distinct polyhedral shape which makes them easy to separate from the eutectic Si, which tend to be located mainly at the interface between dendrites and eutectics. Ca-rich particles are distributed relatively uniformly in the sample [28], and the amounts of UTS, YS, % El including Ca(PO$_4$)$_2$ Al-13Si are 170.18–181.56MPa, 67.29–69.51MPa, respectively, with a related rise in ductility of 8.259–69.51%.

This appears to be a reasonable hypothesis since the nucleation level of Al-Si alloys represents extremely active nuclei, such as AIP and Al$_2$O$_3$. On the other side, CaPO$_4$ additions improved the coarse acicular morphology of eutectic Si, resulting in an increase in the eutectic-nucleation rate, resulting in a fibrous-eutectic Si[29]. The mechanism of this improvement can then be clarified because of the Si phase's increase in growth rate. As the P concentration and, therefore, the amount of AIP particles in the melt is small, most of the Al$_3$Si$_2$Ca that nucleated early during solidification may have infected much of the AIP particles, contributing to a higher-growth rate of the Al-Si eutectic. Such modification strengthens the mechanical properties, improves the overall tensile strength (UTS) and decreases ductility. The reinforcement process occurs from Al$_2$O$_3$ acting as a pinning of dislocation motion, being the amount of influence of multiple reinforcing systems as well as the composition of the alloy. The motion of dislocation happens by contact bond breakage and bond reformation, such that the tolerance for deformation can be strengthened by reducing the probability of movement [30].

Fig. 13(c) displays the impact of Ni(PO$_4$)$_2$ additions on the tensile properties of Al-13Si alloys (UTS, YS, and El). The amounts of UTS, YS, % El including Ni(PO$_4$)$_2$ Al-13Si are 192.11–214.66 and 75.2–78.42 MPa, respectively, with a related rise in ductility of 8.067–8.337%. Eutectic and primary silicon particles are modified and refined with addition of Ni(PO$_4$)$_2$ (0.01–0.03%) and are distributed
uniformly in the matrix. This could be due to the fact that Ni(PO$_4$) reacts with the liquid Al forms AlPO and Al$_3$Ni particles present, which can serve as heterogeneous nucleating sites during the solidification of Al-Si alloys, thus changing primary-silicon particles [10]. The Al$_3$Ni phase is formed in the immediate vicinity of eutectic-Si crystals. Associated temperatures of nucleation and growth of the eutectic and the solidus temperature of the alloy are shifted to lower values [28], displaying fine-sized dimples, instead of the evenly spaced dimples found. The cleavage seen on the surface of the fracture is typical of a fractural fracture. Fig. 13(c) indicates that the introduction of 0.03% Ni(PO$_4$) contributes to large dimples instead of randomly spaced dimples. The fracture analysis of modified-Al-13Si alloys (a) as cast; (b) additive of (Ca$_3$(PO$_4$)$_2$ (c) additive of CuPO$_4$ (d) additive of Ni$_3$(PO$_4$)$_2$.

4. Conclusions
Based on the above, it can be concluded that, firstly, the addition of 0.01% nano-metal-phosphate had a slight change in the eutectic Si, but primary Si was moderately refined. Adding 0.03% of nano-
metal-phosphate to Al-13Si alloy was necessary to reduce primary Si from an average particle size of 16μm to 2μm. Secondly, the addition of various quantities of nano-metal-phosphate in the Al-Si alloy has led to a significant variance in the wear behaviour of the measured Al-13Si. In addition, modification with additional nano-doped metal was observed, resulting in a fine fibrous structure of eutectic silicon, mainly in the addition of CaPO₄ and NiPO₄. After that, results included increased hardness and wear values of modified samples processed by nano-metal-phosphate. In addition, the XRD pattern revealed predominant aluminium, silicon, slight AlP and Al₂O₃ peaks. Finally, results of the cyclic polarisation test showed a susceptibility to micro-pitting corrosion was a dominant characteristic of the Al-Si alloys after being processed by 0.01% of nano-metal-phosphate, while micro-intergranular corrosion in the Al-Si alloys appeared after being processed by 0.03% of nano-metal-phosphate.

References:
[1] R. Haghayeghi; 2008 “Grain Refinement and Nucleation Processes in Aluminium Alloys through Liquid Shearing,” Brunel University.
[2] H. Kim, J. Hong, S. Kim, Y. Park, H. Park, W. Park, J. Kim and K. Buem; 2017 “Effect of silicon on microstructure and mechanical properties of Cu-Fe alloys,” J. Alloys Compd., vol. 707, no. 6, pp. 184–188.
[3] Y. Zuo, Z. Fan, Q. Zhu, L. Lei, and J. Cui; 2013 “Modification of a hypereutectic aluminium silicon alloy under the influence of intensive melt shearing,” Mater. Sci. Forum, vol. 765, pp. 140–144.
[4] D. Li, C. Cui, X. Wang, Q. Wang, C. Chen, and S. Liu; 2016 “Microstructure evolution and enhanced mechanical properties of eutectic Al-Si die cast alloy by combined alloying Mg and La,” Mater. Des., vol. 90, pp. 820–828.
[5] M. Easton, M. Qian, A. Prasad, and D. John; 2016 “Recent advances in grain refinement of light metals and alloys,” Current Opinion in Solid State and Materials Science, vol. 20, no. 1, pp. 13–24.
[6] A. Mazahery and M. Shabani; 2014 “Modification mechanism and microstructural characteristics of eutectic Si in casting Al-Si Alloys: A review on experimental and numerical studies,” Jom, vol. 66, no. 5, pp. 726–738.
[7] S. Gebremeskel, S.Bhatnagar, N. Li, J. Jianping, M. Ludwig, T. Matsubara, Y. Hofer and F. Arnberg; 2016 “Effect of Modifier and Grain Refiner on Cast Al-7Si Aluminum Alloy: a Review,” IOSR J. Mech. Civ. Eng., vol. 5, no. 1, pp. 1–13.
[8] M. Zuo, D. Zhao, Z. Wang, and H. Geng; 2015 “Complex modification of hypereutectic Al-Si alloy by a new Al-Y-P master alloy,” Met. Mater. Int., vol. 21, no. 4, pp. 646–651.
[9] H. Choi and X. Li; 2012 “Refinement of primary Si and modification of eutectic Si for enhanced ductility of hypereutectic Al-20Si-4.5Cu alloy with addition of Al₂O₃ nanoparticles,” J. Mater. Sci., vol. 47, no. 7, pp. 3096–3102.
[10] J. Li, F. Hage, X. Liu, Q. Ramasse, and P. Schumacher; 2016 “Revealing heterogeneous nucleation of primary Si and eutectic Si by AlP in hypereutectic Al-Si alloys,” Sci. Rep., vol. 6, no. April, pp. 1–8.
[11] C. Ho and B. Cantor; 2004 “Modification of hypoeutectic Al-Si alloys,” J. Mater. Sci. Vol., vol. 30, pp. pages1912–1920.
[12] S. Liang and R. Schmid; 2014 “Phosphorus in Al-Si cast alloys: Thermodynamic prediction of the AlP and eutectic (Si) solidification sequence validated by microstructure and nucleation undercooling data,” Acta Mater., vol. 72, pp. 41–56.
[13] A. Haselhuhn, P. Sanders, and J. Pearce; 2017 “Hypoeutectic aluminum-silicon alloy development for gmaw-based 3-D printing using wedge castings,” Int. J. Met., vol. 11, no. 4, pp. 843–856.
[14] W. Kyffin, W. Rainforth, and H. Jones; 2001 “Effect of phosphorus additions on the spacing between primary silicon particles in a Bridgman solidified hypereutectic Al-Si alloy,” J. Mater. Sci., vol. 36, no. 11, pp. 2667–2672.
[15] P. Yan, W. Mao, J. Fan, and B. Wang; 2019 “Simultaneous refinement of primary Si and modification of eutectic Si in A390 alloy assisting by Sr-modifier and Serpentine Pouring Channel Process,” Materials (Basel), vol. 12, no. 19, pp. 1–13.

[16] A. Moffat; 2007 “Micromechanistic analysis of fatigue in aluminium silicon casting alloys, Phd Thesis,” p. p274.

[17] L. Tian, Y. Guo, J. Li, F. Xia, M. Liang, and Y. Bai; 2018 “Effects of solidification cooling rate on the microstructure and mechanical properties of a cast Al-Si-Cu-Mg-Ni piston alloy,” Materials (Basel), vol. 11, no. 7, pp. 3–11.

[18] M. Wang; 2014 “Control of Morphology Al-Fe-Si Phase in Al-Si-Cu Hypoeutectic Alloy,” p. 165.

[19] W. Ebhota and T. Jen; 2017 “Effects of Modification Techniques on Mechanical Properties of Al-Si Cast Alloys,” Alum. Alloy. - Recent Trends Process. Charact. Mech. Behav. Appl.

[20] H. Bartsch, J. Manuel, and R. Grieseler; 2017 “Influence of Nanoscaled Surface Modification on the Reaction of Al/Ni Multilayers,” Technologies, vol. 5, no. 4, p. 79.

[21] H. Medrano, C. Garay, C. Gómez, J. Aguilar, M. Maldonado, and R. Martínez; 2016 “Evolution of microstructure in Al-Si-Cu system modified with a transition element addition and its effect on hardness,” Mater. Res., vol. 19, pp. 59–66.

[22] A. Barros, A. Magno, I. Souza, F. Mota, C. Moreira, A. Silva, M. Rocha and O. Lima; 2015 “Measurements of microhardness during transient horizontal directional solidification of Al-Rich Al-Cu alloys: Effect of thermal parameters, primary dendrite arm spacing and Al2Cu intermetallic phase,” Met. Mater. Int., vol. 21, no. 3, pp. 429–439.

[23] L. Wang, W. Lu, Q. Hu, M. Xia, Y. Wang, and J. guo Li; 2017 “Interfacial tuning for the nucleation of liquid AlCu alloy,” Acta Mater., vol. 139, pp. 75–85.

[24] M. Reboul and B. Baroux; 2011 “Metallurgical aspects of corrosion resistance of aluminium alloys,” Mater. Corros., vol. 62, no. 3, pp. 215–233.

[25] R. Melchers; 2018 “A Review of Trends for Corrosion Loss and Pit Depth in Longer-Term Exposures,” Corros. Mater. Degrad., vol. 1, no. 1, pp. 42–58.

[26] M. Khushaim; 2015 “Investigation of the Precipitation Behavior in Aluminum Based Alloys,” Materials Science and Engineering, King Abdullah University of Science and Technology, November.

[27] M. Kaiser, S. Sabbir, M. Rahman, M. Kabir, And M. Al Nur; 2018 “Effect of Fe, Ni and Cr on The Corrosion Behaviour of Hypereutectic Al-Si Automotive Alloy in 3.5 % NaCl Solution at Different Temperature and Velocity,” Vol. M, No. December, Pp. 11–17.

[28] T. Ludwig, P. Schaffer, and L. Arnberg; 2013 “Influence of some trace elements on solidification path and microstructure of Al-Si foundry alloys,” Metall. Mater. Trans. A Phys. Metall. Mater. Sci., vol. 44, no. 8, pp. 3783–3796.

[29] K. Al-Helal, Y. Wang, I. Stone, and Z. Fan; 2013 “Effect of Ca level on the formation of silicon phases during solidification of hypereutectic Al-Si alloys,” Mater. Sci. Forum, vol. 765, pp. 117–122.

[30] D. Bacon, Y. Osetsky, and D. Rodney; 2009 “Chapter 88 Dislocation-Obstacle Interactions at the Atomic Level,” Dislocations in Solids, vol. 15, no. 09, pp. 1–90.

[31] M. Djurdjevič and M. Grzinčič; 2012 “The Effect of Major Alloying Elements on the Size of Secondary Dendrite Arm Spacing in the As-Cast Al-Si-Cu Alloys,” Arch. Foundry Eng., vol. 12, no. 1, pp. 19–24.

[32] I. Sadeghi, M. Wells, and S. Esmaeili; 2018 “Effect of particle shape and size distribution on the dissolution behavior of Al2Cu particles during homogenization in aluminium casting alloy Al-Si-Cu-Mg,” J. Mater. Process. Technol., vol. 251, no. 11, pp. 232–240.

[33] Y. Yang, R. Jiang, X. Li, Y. Zhang and R. Li; 2019 “Effect of Nanoparticle Content on the Microstructural and Mechanical Properties of Forged and Heat-Treated TiC/2219 Nanocomposites,” J. Chem. Inf. Model., vol. 53, no. 9, pp. 1689–1699.

[34] G. Wignall, R. Rothon, G. Longman, and G. Woodward; 1977 “The structure of amorphous aluminium phosphate by radial distribution functions derived from X-ray diffraction,” J. Mater. Sci., vol. 12, no. 5, pp. 1039–1049.