Modification and Refinement of Al-23Si Alloy Processed by Addition of Nano-Metal-Phosphate

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Abstract. This research investigates the effect of Nano-Metal-Phosphate on Si particles through solidification in hypereutectic Al-Si alloys. Which means the merge of modification and refinement with the addition (0.01-0.03) % of Nano-Metal-Phosphate produced by a stir casting. The process synchronizing effects of Nano-Metal-Phosphate that relates to the AlP and Al₂O₃ formation. These include the following, the effect of Al₂O₃ at the interfaced between the Al phase and Si particles for obstacle the growth and enhance the refinement of the primary Si and the impact of AlP act as sites of heterogeneous nucleation for eutectic Si. Microstructures analysis revealed that both the fundamental and eutectic Si particles were significantly modified and refined. The primary Si grains were refined from star frames to polygon forms, and their edges were more regular. The platelet eutectic Si grains were also modified into the delicate fibrous forms. Resulting in significant ductility enhancement that could have great potential for numerous applications. Besides, studies microstructure and corrosion behaviour by optical and scanning electron microscopy, XRD and electrochemical cyclic polarization.

1. Introduction
Hyper-eutectic Al-Si alloys (higher than 13% Si) have been used in aerospace, military, and automotive applications, particularly in parts such as engine blocks, pistons, and gears, etc. [1,2], due to their excellent good wear resistance, low coefficient of thermal expansion, high resistance to corrosion and castability [3]. Also, functional performance applications require more improved mechanical properties, thermal stability, higher wear resistance, and higher abrasion resistance and wear resistance for heavy-duty Al-Si alloys. It is known that mechanical properties, as well as the manufacturing capacity of Al-Si alloys, depend on a large extent on aluminum morphology, primary and dendrites of silicon, as well as intermetallic phases [4]. Hyper-eutectic of Al-23Si prepared by conventional smelting processes generally contains elementary Si particles and thick eutectic particles in an irregular star shape with increased Si content leading to degradation of mechanical properties, especially ductility [4]. Therefore, the primary particles of silicon must be modified and refined to achieve the best Al-Si hyper-eutectic alloys [5,6].

Much effort has been made to modify the microstructure of Al-23Si alloys by changing process parameters or by adding alloying elements and reinforcements [7]. Among these methods, refinement and modification with phosphorous addition due to its high efficiency [8]. Particles of Si can be further refined in Al-Si alloys by adding Nano-metal-phosphate in the form of primary AlPO₄ alloys. However, it is complicated to achieve the simultaneous modification of the eutectic Si particles, as well as the improvement of the initial Si particles due to the elimination effect [9].
This study is part of a new process to modification and refinement of Al-23Si alloys by adding Nano-Metal-Phosphate to promote mechanical properties, wear behavior, corrosion resistance, and changing its performance. As a result, a complex transformation process is planned, which means combination changes of microstructure (modification and refinement).

2. Experimental Method

2.1. Preparation of Nano-dopant elements

Nano-metal phosphate particles have used an attempt to increase the efficiency of the improvement and modification of eutectic and primary Si partials. But the nanoparticles cannot be obtained from any source; it has been prepared in the laboratory.

One way to prepare Nano-particles is by solid-liquid chemical reaction of powder of elements with phosphoric acid ($H_3PO_4$). Table 1 shows formulas of chemicals reaction of phosphoric acid with powder of elements.

| Material | Formulas |
|----------|----------|
| Fe       | $Fe + 2H_3PO_4 = Fe(PO_4)_2 + 3H_2$ |
| Mg       | $2Mg + 2H_3PO_4 = 2MgPO_4 + 3H_2$ |
| Zn       | $3Zn + 2H_3PO_4 = Zn_3(PO_4)_2 + 3H_2$ |

2.2. Preparation of master alloy

A master alloy was pelleted form consisted of 0.3 g pure aluminum powder and mixing with Nano-Metal-Phosphate and compaction powders under 150 bars to enhance oxidation resistance and flotation. Table 2 defines the particles that compressed together (Nanoparticles and Aluminum powder) elasticity, and then the pressure action leads to permanent bonding at the contact points. The result of compact powder is pellets, which makes it easy to handle.

| Material | Wt.% added | Al-Pure | Compact pressure |
|----------|------------|---------|-----------------|
| Fe(PO_4)_2 | 0.01 g | 0.3 g | 150 bar |
| Mg(PO_4)_2 | 0.01 g | 0.3 g | 150 bar |
| Zn(PO_4)_2 | 0.01 g | 0.3 g | 150 bar |

2.3. Casting Procedures

The Al-23Si alloy produced via liquid metallurgy. Table 3 shows the chemical composition of the aluminum-silicon alloy used in this study. The Al-23Si alloy charge heated to 780°C in the Electric furnace (Carbolite, England). Then degassing by using an inert gas (Argon) followed mechanical agitation with 500 rpm, as shown in Figure 1. At this stage, the dopant-elements which was preheated at 350°C to remove any moisture content and added into the molten alloy. A small amount (0.01-0.03%) of Nano-Metals-Phosphate with particle size (200nm), was inserted into the molten alloy. The agitation of the molten was carried out for about ten minutes to promote uniform dispersion of the nucleant wetting and uniform dispersion of the reinforcement. Then the molten alloy was cast into the preheated steel mold with dimensions 1.5 cm x 15 cm.

| Al | Zn | Ni | Cr | Mg | Mn | Cu | Fe | Si | Element |
|----|----|----|----|----|----|----|----|----|---------|
| Bal. | 0.001 | 0.001 | 0.003 | 0.009 | 0.01 | 0.001 | 0.219 | 23.25 | Content wt. % |

Table 1. Solid-liquid chemical reaction of elements that used in alloying experiments

Table 2. illustrate the composition of pellets.

Table 3 Chemical composition (wt. %) of Al-Si alloy used in this study.
2.4. Microstructural Examination

SEM images of Al-23Si alloy were prepared by grinding with 220, 320, 600, 800, 1000, and 1200 grit papers, respectively. The specimens were then polished with diamond paste, followed by washing and etching by the killer solution. Keller’s reagent is a mixture of NHO$_3$ 5ml, HCl 3ml, and HF 2ml, and H$_2$O 190ml, the solution is used to detect microstructure.

2.5. Hardness Test

Vickers hardness tests (type ZWICK Z323 – Germany) were carried out on the Al-23Si alloy. The load was (0.5Kg) for (10 seconds). Obtaining the average diameter value was taken by three readings for each sample. The equation used to estimate Vickers hardness is:

$$HV = \frac{P}{(D_{AV})^2}$$

where

HV: Vickers hardness number, P: applied load (N), D$_{AV}$: diagonal length (mm)

2.6. X-Ray Diffraction Analysis

The phases present in the modified Al-23Si alloy samples were examined by using X-ray diffraction Shimadzu X-ray Diffractometer (XRD-6000) available at the University of Technology, Nano Technology Center. X-ray Tube: Cu, NF (1.54060 nm), scanning radius: 185mm, Leakage X-rays: less than 2.5μSv/h at maximum out

2.7. Corrosion Tests

The electrochemical examination of the Al-Si alloy was completed with cyclic polarization. All tests were disbursed with a computer-controlled device (PCI4/750, GAMRY, Inc., Warminster, PA) in 3.5% NaCl sol. at 25C. Ag/AgCl as a reference pole and noble metal (Pt) auxiliary pole and working pole used as a specimen holder. The specimen was exposed to 3.5% NaCl solution. The exposure area was 1 mm$^2$. The samples were given a metallographic polishing prior to each test. Specimens were dipped into the solution until obtaining a steady open circuit potential (OCP). The exposed area of the test specimens was about 10 mm$^2$. All data are neutralized according to the surface area. It is calculated by identically identifying the test results using the Echem analyzer[10].

2.8. Wear rate measurement

Dry slip wear tests were performed at room temperature using a laboratory pin on disc wear test with ASTM F732-82 [11]. Nails, which were modified Al-Si alloy o 10 mm and a length 20 mm, were polished by various sheets of grain carbide (220, 320, 500, 800, and 1000), and cleaned with acetone and then dried. The wear equipment consists of a motor with constant rotation speed (510 rpm). The disc is made of tool steel with a hardness of 65 HRC. Relative mass changes were tested by weighing the samples before and
after wear using a digital scale according to the sensitive scale classification (DENVER Tool, Japan) (Max-210gm) at 0.0001 mg. The applied loads were 500 kN. The disc is cleaned after each test. The following equation is 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)

### 3. Results and Discussion

#### 3.1. Microstructure of Experimental Materials

Figure 2 shows microstructures of unmodified Al-23Si alloy. Initially, composed of large grains of primary Si and platelet eutectic Silicon with grain size equal to 87 micro-meters by use J-Image program.

Figure 3a and 3b show microstructures of Al-23Si after additive Nano-iron phosphate. They are composed of fine grain size equal to 33 micro-meters by added 0.01 Nano-iron phosphate. Addition 0.03% concentrations of Nano-iron phosphate may act as a promoter for grain refinement of primary Si and modifier eutectic Si grains size equal to 26 micrometers. However, considering the damaging effects of iron, Nano-Iron phosphate can enhance the precipitation of Fe-rich particles or change the morphology of the phases, which are less detrimental than needles by addition 0.03% of Nano-Iron phosphate[11]. Observing the basic microscopic structure of all experimental materials revealed that it consisted of an alpha dendrite (a mechanical mixture of alpha) and a different intermetallic compound. Figure 4(a,b) shows microstructures of Al-23Si after additive of 0.01 and 0.03% of Nano-magnesium phosphate. Composed of fine grains with a size equal to 35 micrometers and 24 micrometers, respectively. The α phase precipitation of the liquid as a preliminary step in the form of dendrites, consisting of Al and MgP in AlMg, AlP, and Al₂O₃ alloys. The size of finer dendrites is similar for each case of our experiment alloys, but the secondary dendrite arm space (SDAS) is a little different. AlP and Al₂O₃ particles are like Spherical grains. However, thickened grains were observed on the borderline of α-phase dendrites.

Figure 5a and 5b show microstructures of Al-23Si after additive 0.01 and 0.03% of Nano-zinc phosphate. The structure of Al-ZnP cast alloys formed from α, AlP and Al₂O₃ particles [7][12]. The primary Si precipitates from the liquid α-Al in the form of dendrites and nominally include Al and Zn. The fine size of the dendrites is similar to all experimental alloys. On the edge of the bifurcations in the alpha stage, small round granules are observed. Zin containing stages, such as AlZn, is formed, especially between alpha bifurcations. On the edge of the bifurcations in the alpha stage, small round granules are observed. Zin containing stages, such as AlZn, is formed, especially between alpha bifurcations. Results have proven that as the phosphate content increases, the bifurcation length and space increase a fine arm. Because these alloys, despite their zinc content, belong to typical alloys, because they have a similar microscopic structure.
Figure 2. Microstructures of unmodified Al-23Si alloy

Figure 3. Microstructures of Al-23Si after additive of Nano-iron phosphate (a) 0.01 and (b) 0.03%.

Figure 4. Microstructures of Al-23Si after additive of Nano-magnesium phosphate (a) 0.01 and (b) 0.03%.
3.2. Mechanical Properties

Figure 6 shows the relationship between the hardness value of the unmodified Al-23Si alloy and modified Al-23Si alloy with different weight percentages of Nano-metal Phosphate. It has been found that the Nano Al_2O_3 exhibit higher hardness than the as-cast alloy. The hardness value of the modified Al-23Si alloy increased with increasing the ratio of the Nano-metal Phosphate. This due to the grain refinement occurs when a large amount of Al_2O_3 is presented as a result of the reaction of the Nano-metal-Phosphate with the molten and grain boundary suffers pinning[1].

When added 0.03 %, Nano-metal-Phosphate with particle size of 200nm exhibit slightly higher hardness when compared with the addition 0.01 % particles. The increases in the hardness of the Al-23Si alloy due to Al_2O_3 and intermetallic phases can be related to the rise of mechanical properties.

![Figure 6](image)

**Figure 6.** Show comparable hardness with the content of Nano-metal phosphate types.

3.3. X-Ray Analysis

Figure 7 shows X-ray diffraction pattern characteristic (111), (200), (220), and (311) face-center-cubic α-Al peaks, Besides the cubic peak of Si (111), which proposes mixtures in two stages, Si is entirely insoluble in phase Al. When the dopants in α-Al solubility are exceeded during solidification. Peaks were detected of intermetallic phases of AlFe, AlMg, AlZn, and Al_2O_3 because of the alloy changed monotonously [13].
During solidification of the molten metal, there are preferred orientations in which a fraction of the grains grow faster than others, i.e., the formation of crystallographic texture. This crystallographic texture is controlled by the processing technique, solidification, deformation, annealing, and phase transformation. A textured material is one where the crystallites occupy a preferential orientation, whereas a texture-less material is when the orientations are generally random. Since Al is an FCC metal, columnar grains usually have <100> axes, i.e., fiber texture in the <100>. The texture is categorized as macro-texture and micro-texture. [14,15].

3.4. Wear Behaviour
The relationship between addition Nano-metal-Phosphate and wear rate of experiments alloys are presented in Figure 8. The wear rate decreases with an increase in the percentage of Nano-metal-Phosphate particles. Furthermore, the relationship is linear. This means, decreases of grain size and proper distribution of primary Si, eutectic and intermetallic phases, wear rate decreases regardless of the reinforcement Nano Al$_2$O$_3$ size and percentage. Also, wear and tear rate of processed composites decreases with increasing modifier elements (Nano-Metal-Phosphate). The improved wear resistance to casting procedure is referred to the distribution of particles within the base Al and refinement of grain.

Figure 7. XRD Pattern for Al-23Si Samples processed by different Nano-Metal Phosphate.
Figure 8. The Variation of Wear Rate with Sliding Time at Different types of Nano-Metal Phosphate.

Figure 9. Optical Micrographs of Worn Track: (A) As Cast; (B) Additive of Nano-Iron Phosphate (C) Additive of Nano-Magnesium Phosphate (D) Additive of Nano-Zinc Phosphate.

Figure 9 shows the optical micrograph of the worn surface of stir processed composites. The micrograph reveals that the worn track breadth decreases in modified alloy compared to unmodified alloy. It's proof that the extent of wear and tear in the composite is below that of unmodified alloy. The depth and breadth of the grooves generally imply that associate in the foster quantity of fabric off from the specimen surface [16]. It is expected that the uniform distribution of particles and the modification of Si grains can cause a high wear resistance.

3.5. Corrosion Behavior

In order to estimate the polarization field for analysed Al-23Si alloys, the cyclic polarization curves showed all three potential domains, namely: cathodic field, the passive field, and the trans-passive field. The larger passive field and the smaller value of current density in the trans-passive field show a higher corrosion resistance for the analysed alloys [3]. Pitting was detected preferentially in the unmodified alloy. The scale and density of pits are growth with the Al-23Si.
Figure 10. Cyclic Polarization of Al-23Si alloy Curves in 3.5 % NaCl Sol. (A) As Cast (B) Additive of Nano-Iron Phosphate (C) Additive of Nano-Magnesium Phosphate (D) Additive of Nano-Zinc Phosphate.

Cyclic Polarization and respectively determined to pit corrosion rates for an Al-23Si alloy covered with a semi-conductive passive film [17,18]. The cyclic polarization curve of Al-23Si displays active dissolution near $E_{\text{corr}}$, followed by a definite increase in the current with the applied potential due to weakening and thinning of the passive layer as a result of the aggressive attack of Cl$^-$ anions as shown in Figure 11a.

Also, in Figure 10, the cyclic polarization curves display anodic behaviour. This was clear in the $E_{\text{corr}}$ branches of Al with added phosphate elements, which showed some, arrange of curvature over the whole applied potential range.
Pitting corrosion initiates at the interface between the $\alpha$-Al matrix and the Fe-rich intermetallic as a result of micro-galvanic corrosion processes. Alloys were suffered by general irregular corrosion, and their surface was covered by grey corrosion rust\cite{4}.

Observations by the microscopic proven the significant activity of Al-FeP compared to unmodified alloy corrosion. The segregation at the grain boundaries leads to intergranular effects and galvanic corrosion. The estimate of the Al-FeP surfaces after exposure to corrosion solution by utilize microscopy shows that on the surface, there are places with micro-localized corrosion Figure 10b. Figure 11(c, d) shows microscopic observations that demonstrate a high passivity of Al-ZnP and Al-MgP compared to non-modified Al-23Si corrosion alloys. Additionally, Al-ZnP and Al MgP to Al-23Si alloys, oxide layer tend to grow and passivate with low current and wide potential range. These results reflect the high passivity and higher tendency to resist in 3.5%NaCl solution, the anodic polarization curve displayed perfect passive layer, referring to its high pitting corrosion resistance. The passivity of Al-23Si alloys continued up to reaching pitting potential ($E_{pit}$). Notable changes occurred within the very narrow passive region at potentials exceeding ($E_{pit}$). These involved not increase in current density and formation of a smaller or no loop of hysteresis on the potential adverse curve. These results were a clear sign of withstanding layer passivity, and the initiation and propagation of pitting corrosion\cite{4,19}.

4. Conclusions
   1. Castings of Al-23Si alloy matrix was produced by additives of Nano-Metal-phosphate.
   2. The fine microstructure, primary elliptical silicon particles and the circular shape of eutectic are obtained by new technique.
   3. A suitable distribution of reinforcement particles ($Al_2O_3$ and intermetallic compound) has been achieved.
   4. The X-ray analysis shows the main peaks of Al and Si and the minor peaks of AlP, $Al_2O_3$, and Al-rich intermetallic phases.
   5. Hardness is increasing of Al-23Si that processed by Nano-metal-phosphate increased due to the formation of intermetallic compounds.
6. The corrosion resistance is increasing of Al-23Si processed by Nano-metal-Phosphate in NaCl solution that affected by microstructure, and oxide film grows.

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