Refinement effect of Zirconium and Samarium on Al-4Mg cast alloy

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Abstract

This study aims at investigating the modification response of cast Al-4%Mg alloy to Zirconium or Samarium additions at high and low levels. Thermal analysis was used to evaluate the influence of Zirconium and Samarium. The solidification data represented the four main reaction peaks during solidification and had shown that both Zr and Sm play a role in refinement with a depression in solidification temperature. Moreover, Sm acts as a modifier as it had noticeable effect on retarding the recrystallization temperature. Microstructure Examination was implemented by optical microscopy, image analysis software and scanning electron microscopy (SEM) with the aid of image analysis and Energy Dispersive x-ray spectroscopy (EDS). The results revealed the formation of new intermetallic phases such as agglomerates of Al$_{18.76}$MgZr$_{0.04}$Ti$_{0.52}$Fe$_{0.07}$ and Chinese script shapes of Al$_{25.38}$MgFe$_{2.77}$Sm$_{1.48}$. Accordingly, a noticeable grain size reduction is found with respect to the level of addition of Zr and Sm when showed more refinement effect.

1. Introduction

Al–Mg alloys containing Mg up to 10 wt.% exhibit excellent corrosion resistance, good weldability and machinability [1]. These alloys are mainly used in marine atmosphere applications and in food and beverage industries, in addition to others such as decorative applications. However, the range of their applications is widening by time which demands further enhancement in their mechanical performance. These improvements can be achieved by adding minor alloying elements which enables the control of grain size and morphology.

Zirconium is one of the transition elements used as additions (up to 0.5 wt.%) to the aluminum alloys for the purpose of microstructure control by grain refining and, hence, improving the mechanical properties. Feng Wang et al [2] studied the mechanism of grain refining by zirconium additions to cast aluminum alloys, while Abdelaziz et al [3] reported improvement of mechanical properties of A354 alloy (Al–Si–Cu–Mg) upon adding 0.3 wt.% of Hui Qian et al [4] found considerable reduction in size with homogenous dispersion of the Si particles in Al-Si alloys, as the mechanical properties were substantially improved and the fractured surface showed more plastic deformation.

Rare earth elements are also shown by various investigations to play a great role in microstructure modification, consequently, enhancing mechanical properties of aluminum alloys. Nie et al [5] and Nogita et al [6] concluded, through studying the impact of alloying with various rare earth elements, that Er has the greatest influencing effect in modifying Al–Si alloys. Nie et al [5] investigated the influence of Er addition on Al–Mg, Al–Cu, Al–Zn–Mg, Al–Zn–Mg–Cu, Al–Li alloys and their main conclusion was that as Er content increases, it promotes the formation of high melting point Al3Er particles which act as sites for heterogeneous nucleation and result retardation of grain coarsening. In Al–Cu alloys the formation of low melting point Al$_6$Cu$_4$Er phase is promoted, which reduces the hardening effect. Nogita [6] studied the influence of (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) additions on Al–10 Si alloy and they found that Er has the highest modification effect, and the finest Si fibrous particles were obtained. Tsai et al [7], Tash et al [8] and Mahmoud et al [9] investigated the influence of Ce and La with different proportions on Al–7Si–0.3Mg, Al–12Si–2.5Cu–0.4Mg and A413.1 respectively, and reported modification in the eutectic Si particles as their size was refined and their shape became more rounded. Zhang et al [10] used mixtures of Ce and La additions and they found a notable reduction
in grain size and secondary dendrite arm spacing (SDAS) and the mechanical properties were improved when the addition was up to 1 wt.%. Li et al [11], Qiu et al [12], Zhi Hu et al [13] and D. Fredian et al [14] studied Samarium addition effect on Al-12Si, Al-20Si, Al-Si-Cu and Al-5Zn-0.5Si, respectively. They reported major refining effect on silicon particles and reduction in SDAS. However, Qinglin Li [11] and Qiu [12] observed that the maximum beneficial Sm content is 0.6 wt.% whereas beyond this level coarsening effect will take place, while Zhi Hu [13] found degradation in mechanical properties if Sm content exceeds 1 wt.%. Both Zirconium and Samarium additions affect the structure morphology and chemical composition of the formed intermetallic phases during aluminum alloy solidification as they have limited solubility in $\alpha$-Al matrix phase. Feng Wang et al [2] attributed the contribution of Zr refining effect to the formation of metastable Al$_3$Zr on grain boundaries which resist grain growth. Similar results were achieved by Hui Qian et al [4] as they found small shining particles of Al$_3$Zr precipitated along the grain boundaries in which grain refining took place. Li et al [11] reported the generation of non-homogenous distributed bright particles of Al$_5$SiSm compound which caused a hinderance in grain growth during the stage of recrystallization. Similarly, D. Fredian et al [14] observed the intermetallic phase Al$_3$Si$_2$Sm in the interdendritic region. Zhi et al [13] found that when Sm content exceeds 1.5%, there would be a formation of two shapes of intermetallic phases; the first shape was a needle of Al$_8$SiSm intermetallic phase while the second shape was a plate of Al$_3$Si$_3$CuSm$_3$ intermetallic phase.

Despite the significant results obtained by previous researchers, further work is needed to investigate the thermal effect of the various additions. The additions cause their effect through refining by inducing nucleation and/or entering into new phases/structures formation. The understanding of both roles could be shown by studying their thermal effects during the alloy solidification. Thermal analysis is based on the study of temperature change during solidification in the casting process, the resulted solidification data can be useful in detecting the changes of solidification behaviour and the effect of refining or modification of the additives. In Al-Si alloys, the growth models proposed for modifying eutectic Si are impurity induced twinning (IIT) and twin plane re-entrant edge (TPRE) mechanisms [15, 16]. In the IIT mechanism, the clusters of modifier atoms are absorbed into the growth steps of Si at the solid melt interface inducing a high density of twinning. However, in TPRE mechanism, the clusters of atoms are absorbed at the TPRE poisoning the Silicon crystals and resulting in branching of Si structures [17]. The grain refinement achieved by Zr addition results from the formation of the Al$_3$Zr particles formed by peritectic reaction. Al$_3$Zr provides heterogeneous nucleation sites and constitutional undercooling conditions for $\alpha$-Al [17]. The current study focuses on the thermal analysis study of the relevant solidification data and morphological characterization through microstructural observations of the alloy Al-4Mg with added low and high levels of Zr or Sm.

### 2. Materials and methodology

The chemical composition of the alloys used in the current study are presented in table 1. The main raw materials used in the study are high purity aluminum (99%), master alloy of Al-10% Mg and master alloy of Al-5%Ti-1%B (as grain refiner). Zirconium and Samarium were used as additives. The weighed materials were mixed in a SiC crucible inside an electrical resistance furnace where the temperature was maintained at $760 \pm 5$ °C. The melt was stirred by carbon rods to keep its homogeneity. Degassing was performed for at least 10 min by injecting Argon gas to remove entrapped gases in the melt this was followed by skimming the oxide layer on the melt surface prior to casting.

Before casting the molten metal, the graphite mold was preheated in an electric furnace at 700 °C. That step was taken to keep the cooling rate as minimum as possible (0.3 °C–0.5 °C s$^{-1}$) so more accurate analysis data could be extracted during melt solidification. After 30 min of graphite mold preheating, the melt was poured in it immediately and a thermocouple of K-type was connected from the top of the graphite mold through a plate of insulating ceramic to data acquisition system device (Data Translation—DT 9828) linked to a computer and

| Alloy       | Mg    | Fe    | Si    | Cr    | Ti     | Al    | Zr   | Sm   |
|-------------|-------|-------|-------|-------|--------|-------|------|------|
| Base        | 3.223 | 0.33  | 0.392 | 0.156 | 0.067  | 95.803| 0.0  | 0.0  |
| Base + low Zr | 4.168 | 0.342 | 0.588 | 0.149 | 0.026  | 94.58 | 0.2  | 0.0  |
| Base + high Zr | 4.048 | 0.317 | 0.545 | 0.164 | 0.037  | 94.695| 0.5  | 0.0  |
| Base + low Sm | 3.826 | 0.367 | 0.585 | 0.167 | 0.059  | 94.962| 0.0  | 0.5  |
| Base + high Sm | 3.781 | 0.346 | 0.512 | 0.194 | 0.037  | 94.898| 0.0  | 1.0  |
recording temperature—time data from which the cooling curve is generated. The frequency of data plotted is 10 Hertz (i.e. data is generated every 0.1 s).

In order to study the microstructural features of the castings prepared, the samples were sectioned; polished using alumina powder of particle size 3 μm; and then etched by Keller’s reagent (2%–3% nitric, 1%–2% hydrochloric and 1% fluororic acid). The examination of the microstructure was implemented by both optical microscopy (Olympus BX-53M connected to a computer with image analysis software- Olympus stream installed) and scanning electron microscopy (SEM) with the aid of image analysis and Energy Dispersive x-ray spectroscopy (EDS). All these observations were recorded for the same solidification rates during thermal analysis. Grain size measurements were executed by Image J software. A scanning electron microscope (Inspect S50) equipped with an energy dispersive x-ray spectrometer (EDS) was used for micro elemental analysis and generation of elemental mapping as a function of local concentration of elements.

3. Results and discussions

3.1. Thermal analysis and solidification data

The data acquisition system was used to generate temperature—time cooling curves showing first and second derivatives indicating the peaks for the corresponding phase reactions, for each casting trial. The first derivative represents the slope of the cooling curve (i.e. cooling rate) so when first derivative increases, that indicates a generated latent heat due to new phases formation. Second derivate facilitates the detection of phases through accurate determination of nucleation temperatures formed during the solidification process. The four significant peaks correspond to the formation of the four main phases according to Backerud [18]. The observed reactions during solidification are due to the formation of α-Al dendritic matrix (Peak 1), followed by formation of grey needle form of Al3Fe precipitates (Peak 2), followed by precipitation of Mg2Si particles (Peak 3). Finally, a complex eutectic (Al3Fe, Mg2Si, Al8Mg5 and Al) is formed at the end of solidification (Peak 4).

The following terms were defined and extracted from each peak: Nucleation temperature T(N) is the first noticeable change in the derivative of the cooling curve at which nucleation behavior changes as observed through the heat flow, it indicates the beginning of α-Al dendritic matrix formation. T(M) is the solidification reaction temperature, which is the minimum temperature that can be reached before recalescence. Growth temperature T(G) is that reached after recalescence. By the end of solidification, the temperature T(S) corresponds to the end of α-Al dendritic phase solidification. These terms of temperature and time were extracted from the solidification curves and presented in comparative charts.

Figure 1 shows the resulting cooling curves for the Al–4Mg base alloy, base alloy with low Zr, base alloy with high Zr, base alloy with low Sm and base alloy with high Sm; from which it is shown that their solidification cooling rates are 0.23 °C s⁻¹, 0.34 °C s⁻¹, 0.31 °C s⁻¹, 0.42 °C s⁻¹ and 0.49 °C s⁻¹, respectively. This shows that the solidification cooling rates are in the accepted range for determining solidification reactions. The base alloy and the alloy with high Zr content are so different from other alloys due to their lower solidification cooling rate and this can be related to the reduced preheating temperature of the graphite mold, which ranged from 600–650 °C.

Figure 2 shows the comparison of the solidification data extracted from thermal analysis; from which the four formed peaks are revealed from the first derivatives for the cooling curves. Figures 2(a)–(e) represent the base alloy, base alloy with low Zr, base alloy with high Zr, base alloy with low Sm and base alloy with high Sm; respectively.

Table 2 shows the nucleation temperature T(N), nucleation time t(N), solidification reaction temperature T(M), solidification reaction time t(M), growth temperature T(G), growth time t(G) end of solidification temperature T(S) and end of solidification time t(S). As for the peaks corresponding to the nucleation temperatures T(N), the addition of low Zr content led to an increase of the height of the peaks (2, 3 and 4) by 13 °C, 8 °C and 4 °C; respectively. While the first peak was slightly decreased by 1.7 °C. For the high Zr content, it resulted a depression for peaks (1, 2 and 3) by 1.7 °C (same as low Zr addition), 25 °C and 12 °C, respectively, while peak (4) has remained the same. It is noticed from the same table 2, that low Sm addition has slightly reduced peak (1) height by 2 °C, while high Sm content reduced its height by 1.5 °C. Both low and high content of Sm caused nearly same reduction values for peaks (2, 3 and 4) by 20 °C, 28 °C and 14 °C; respectively.

The peaks corresponding to the start of solidification reaction temperatures T(M) maintained the same value for peak (1) as that of the base alloy except only the high Sm addition which led to reduction by 1 °C. The addition of low Zr content increased the peaks (2 and 3) by 12 °C and 4 °C; respectively, while the high Zr content depressed the same peaks by 29 °C and 12 °C; respectively. Both low and high Zr content resulted the fourth peak at the same value. The addition of both low and high content of Sm decreased the peaks (2, 3 and 4) by about 25 °C, 32 °C and 12 °C; respectively.
Figure 1. Cooling curves for Al-4Mg base alloy, Base + low Zr, Base + high Zr, Base + low Sm and Base + high Sm. The resulted total solidification cooling rates are 0.23 °Cs⁻¹, 0.34 °Cs⁻¹, 0.31 °Cs⁻¹, 0.42 °Cs⁻¹ and 0.49 °Cs⁻¹ respectively.

Figure 2. Solidification curves, their first and second derivatives obtained and the main reactions observed during solidification, (a) for Al-4Mg base alloy, (b) for Al-4Mg-0.2Zr, (c) for Al-4Mg-0.5Zr, (d) for Al-4Mg-0.5Sm, (e) for Al-4Mg-1Sm. Phases formed as following: Peak #1: α-Al matrix. Peak #2: Al₃Fe precipitates. Peak #3: Mg₂Si particles. Peak #4: complex eutectic of Al₃Fe, Mg₂Si, Al₅Mg₄ and Al.
| Alloy          | Peak no. | T<sub>(s1)</sub> | t<sub>(s1)</sub> | T<sub>(s2)</sub> | t<sub>(s2)</sub> | T<sub>(c1)</sub> | t<sub>(c1)</sub> | T<sub>(c2)</sub> | t<sub>(c2)</sub> | ∆T = T<sub>(c1)</sub>−T<sub>(c2)</sub> | ∆t = t<sub>(c1)</sub>−t<sub>(c2)</sub> | SCR = ∆T/∆t |
|---------------|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|----------|
| Base          | 1        | 641.7           | 67.1            | 639.5           | 72.5            | 639.7           | 77.0            | 639.6           | 80.1            | 2.1             | 13.0            | 0.16          |
|               | 2        | 627.0           | 215.0           | 626.3           | 219.7           | 603.5           | 244.9           | 23.5            | 29.9            | 0.79            |                 |             |
|               | 3        | 603.5           | 323.4           | 600.6           | 333.7           | 572.4           | 400.9           | 31.1            | 77.5            | 0.40            |                 |             |
|               | 4        | 572.4           | 400.9           | 567.3           | 410.3           | 556.3           | 430.5           | 16.1            | 29.6            | 0.54            |                 |             |
| Base + Low Zr | 1        | 639.9           | 30.4            | 639.6           | 31.9            | 639.7           | 34.1            | 639.7           | 34.7            | 0.2             | 4.3             | 0.04          |
|               | 2        | 639.6           | 35.5            | 639.5           | 37.0            | 639.2           | 42.8            | 1.0             | 17.3            | 0.06            |                 |             |
|               | 3        | 611.3           | 186.4           | 604.2           | 204.7           | 594.5           | 227.1           | 16.8            | 40.7            | 0.41            |                 |             |
|               | 4        | 576.6           | 261.8           | 566.9           | 271.0           | 553.0           | 290.6           | 23.6            | 28.8            | 0.82            |                 |             |
| Base + High Zr| 1        | 640.0           | 53.7            | 639.2           | 56.5            | 639.3           | 58.7            | 639.1           | 62.8            | 0.9             | 9.1             | 0.10          |
|               | 2        | 601.7           | 266.0           | 597.1           | 279.1           | 591.8           | 293.5           | 9.9             | 27.5            | 0.36            |                 |             |
|               | 3        | 591.8           | 293.5           | 588.7           | 300.7           | 572.1           | 332.8           | 19.7            | 39.3            | 0.50            |                 |             |
|               | 4        | 572.1           | 332.8           | 567.1           | 340.8           | 541.9           | 379.7           | 30.3            | 46.9            | 0.64            |                 |             |
| Base + Low Sm | 1        | 639.6           | 21.4            | 639.5           | 24.0            | 639.5           | 25.1            | 639.4           | 28.2            | 0.1             | 6.8             | 0.02          |
|               | 2        | 606.8           | 143.7           | 599.5           | 157.6           | 589.7           | 174.6           | 17.1            | 30.9            | 0.55            |                 |             |
|               | 3        | 575.4           | 193.7           | 569.0           | 202.2           | 561.7           | 212.9           | 13.7            | 19.2            | 0.71            |                 |             |
|               | 4        | 558.6           | 216.9           | 554.6           | 222.1           | 549.8           | 228.3           | 8.8             | 11.4            | 0.77            |                 |             |
| Base + High Sm| 1        | 639.1           | 20.1            | 638.6           | 24.0            | 638.6           | 24.8            | 638.5           | 31.6            | 0.7             | 11.5            | 0.06          |
|               | 2        | 608.1           | 129.6           | 603.9           | 138.7           | 594.0           | 156.4           | 14.1            | 26.8            | 0.33            |                 |             |
|               | 3        | 576.3           | 177.5           | 567.5           | 188.0           | 561.9           | 196.0           | 14.5            | 18.5            | 0.78            |                 |             |
|               | 4        | 558.6           | 200.1           | 555.0           | 204.8           | 549.3           | 212.5           | 9.3             | 12.4            | 0.75            |                 |             |

N.B. Phases formed:
1: α-Al matrix.
2: Al<sub>3</sub>Fe precipitates.
3: Mg<sub>2</sub>Si particles.
4: complex eutectic of Al<sub>3</sub>Fe, Mg<sub>2</sub>Si, Al<sub>8</sub>Mg<sub>5</sub>, and Al.
For the peaks corresponding to the end of solidification reaction temperatures T(S), the first peak is formed at the same value as that of base alloy regardless of the addition condition. The addition of low Zr content brought a sharp rise for peaks (2 and 3) by 35 °C and 22 °C, respectively, while peak (4) was slightly decreased by 3 °C. The additions of low and high Sm content decreased peak (2) by 14 °C and 9 °C; respectively, peaks (3 and 4) were decreased by 11 °C and 7 °C; respectively for both low and high Sm content additions.

For the sake of interpreting the significance of these solidification data on refining and modification response, a correlation between solidification reaction temperatures T(M) and grain refinement is made. It is observed from table 2 that the addition of Zr or Sm led to drop in T(M), where the maximum reduction is found for the high level Sm addition. As for the modification response, the undercooling parameter (∆T) or the recalescence (which is the difference between growth temperature T(G) and solidification reaction temperature T(M)) indicates the changes in the grains morphology; as less ∆T values result more equiaxed shape and enhanced modification. The recalescence measured for Al-4Mg base alloy, base alloy with low Zr, base alloy with high Zr, base alloy with low Sm and base alloy with high Sm are 0.2 °C, 0.1 °C, 0.1 °C, 0.0 °C and 0.0 °C; respectively.

3.2. Microstructural observations

Figure 3 shows typical examples of optical microstructures for Al-4Mg base alloy with low and high Zr or Sm additions. The microstructure reveals the presence of intermetallics of Chinese script morphology with high Sm addition. Figure 4 illustrates the SEM micrographs for the Al-4Mg base alloy. The EDS analysis at point (A) in the Al matrix, as shown in figure 4(b), suggests the presence of Al_{22.3}MgFe_{0.0}Si_{0.0} in the matrix, which indicates that Mg and traces of Fe and Si have formed a solid solution with the Al matrix. The EDS spectra taken for points (B, C) in figures 4(c), (d) show that the elements Mg, Fe and Ti have formed Al_{48.13}MgFe_{1.33}Ti_{0.12} intermetallics and the elements Mg, Fe and traces of Si have formed Al_{1.48}MgFe_{4.63}Si_{0.06} intermetallics; respectively. For more illustration, X-ray elemental mapping images for Fe, Mg, Si, Al, Cr and Ti were generated for the Al-4Mg base alloy and are shown in figures 5(a)–(f), it is apparent that Mg, Fe and Ti take part in the formation of intermetallics.

After establishing the structural details for the base alloy, the following section will discuss the induced changes resulting from the additions. As for the effect of Zr additions, figures 6 and 7 represent the SEM micrographs for Al-4Mg-0.2Zr and Al-4Mg-0.5Zr alloys; respectively. For Al-4Mg-0.2Zr alloy, the EDS analysis of point (A) in the Al matrix as shown in figure 6(b) was identified to be Al_{24.46}Mg which points out that Mg forms a solid solution with Al matrix. The EDS spectra taken for points (B, C) in figures 6(c), (d) show that the elements Mg, Fe and traces of Zr form Al_{41.7}MgFe_{10.4}Zr_{0.02} intermetallics and the elements Mg, Zr and traces of Ti form Al_{17.0}MgZr_{1.37}Ti_{0.11} intermetallics; respectively. For Al-4Mg-0.5Zr alloy, the analysis of EDS for point (A) in the Al matrix as shown in figure 7(b) was identified to be Al_{27.0}MgFeSiZr_{0.014} which points out that Mg and traces of (Fe, Si, Zr) form solid solution with Al matrix. The EDS spectra taken for points (B, C) in figures 7(c), (d) show that the elements Mg, Zr, Ti and traces of Fe form Al_{88.7}MgZr_{7.0}Fe_{0.07} intermetallics and the elements Mg, Fe with traces of Si form Al_{24.33}MgFe_{2.33}Si_{0.04} intermetallics; respectively. For more illustration, X-ray elemental mapping images for Fe, Mg, Si, Al, Zr and Ti were generated for the Al-4Mg-0.5Zr alloy and are shown in figures 8(a)–(f) and 9(a)–(f) respectively, it is apparent that Mg, Fe, Zr and Ti take part in the formation of intermetallics.

For the effect of Sm additions, figures 10 and 11 represent the SEM micrographs for Al-4Mg-0.5Sm and Al-4Mg-1Sm alloys; respectively. For Al-4Mg-0.5Sm alloy, the EDS analysis of point (C) in the Al matrix, as shown in figure 10(d), suggests the matrix to be a solid solution of Al_{20.1}MgFe_{0.03}Sm_{0.008} which points out that Mg with traces of Fe and ignorable traces of Sm form solid solution with the Al matrix. The EDS spectra taken for points (A, B) in figures 10(b), (c) show that the elements Mg, Fe with traces of Sm also takes part in forming Al_{18.77}MgFe_{1.4}Sm_{0.02} crossing sticks (near to Chinese script) intermetallics and the elements Mg, Fe and Sm forms Al_{19.4}MgFe_{1.5}Sm_{0.82} intermetallics; respectively. For Al-4Mg-1Sm alloy, the analysis of EDS for point (A) in the Al matrix, as shown in figure 11(b), suggest similarly that it is Al_{19.41}Mg which points out that Mg forms a solid solution with the Al matrix. The EDS spectra taken for points (B, D) in figure 11(d) shows that the elements Mg, Fe and Sm form Chinese script shape of Al_{32.23}MgFe_{2.77}Sm_{1.48} and Al_{32.42}MgFe_{1.42}Sm_{0.71}Si_{0.05} form intermetallics; respectively. Also, the EDS analysis of point (C) in figure 11(c) shows that the elements Mg and Si form dark shape AlMgSi_{0.65} intermetallics. For more illustration, X-ray elemental mapping images for Fe, Mg, Si, Al, Sm and Ti were generated for Al-4Mg-0.5Sm and Al-4Mg-1Sm alloys and are shown in figures 12(a)–(f) and 13(a)–(f); respectively, it is apparent that Mg, Fe, Sm, Ti and Si (which is observed in EDS spectra for the Al-4Mg-1Sm alloy) take part in the formation of intermetallic phases.
3.3. Grain refining

Figure 14 shows typical examples of optical microstructures for Al-4Mg base alloy with low and high Zr or Sm additions. The microstructure reveals the reduction in grain size according to the level of addition of Zr or Sm. Grain refinement by zirconium is achievable at an addition level much lower than the proposed peritectic composition for the binary Mg–Zr system under slow cooling rate. Nearly equiaxed grains were obtainable at 0.22%Zr content, which is a result of both undissolved zirconium particles acting as heterogenous nucleation sites and dissolved zirconium acting as a dispersion element for growth restriction [19, 20]. A uniform, fine and equiaxed grain structure was achieved by adding Zr to peritectic aluminum alloys [2, 21]. Baradarani et al [22] reported that adding Zr also shows a grain refinement influence on Al–Si alloys. Although the kinetics and thermodynamics interactions between Sm and Al–Mg alloys are still unknown; grain refinement by samarium can be confirmed as it reduced SDAS in previous researches. Equiaxed grains and low aspect ratio for silicon particles were observed upon adding samarium (up to 0.6%) for Al-7Si-0.7Mg alloy. The grain size measurements for Al-4Mg with added low and high Zr or Sm are recorded in table 3. It is obvious that more grain refining is achieved as the level of addition increases. The high Sm level shows more effect on grain size reduction and the generation of equiaxed grains in the Al-4%Mg alloy is conducted through adding zirconium or samarium.

Figure 3. Optical micrograph at magnification 100X which were taken for: (a) Al-4Mg base alloy, (b) base + low Zr, (c) base + high Zr, (d) base + low Sm, (e) base + high Sm.
4. Conclusions

The following points are concluded from the solidification data and microstructural observations on the Al-4Mg base alloy with addition of low and high levels of Zr or Sm:

Figure 4. SEM micrograph taken from Al-4Mg base alloy showing intermetallic precipitations. (a) SEM micrograph, (b)–(d) EDS spectra of points A, B, and C in (a), where the matrix analysis ($Al_{22.35}Mg_{6.36}Fe_{0.03}Si_{0.04}$) (point A), the precipitations of ($Al_{48.15}Mg_{11.33}Fe_{11.33}Ti_{1.11}$) (point B) and ($Al_{31.48}Mg_{4.63}Fe_{4.63}Si_{0.06}$) (point C) intermetallics.

Figure 5. X-ray images of Fe, Mg, Si, Al, Cr, Ti (a)–(f) corresponding to backscattered image (CP) taken from Al-4Mg base alloy, the AlMgFeTi rich intermetallic phase particle observed.
1. Sm and Zr additions resulted in refinement in the grain size of Al-4Mg Alloy by values ranging from 45–100 μm.

2. A maximum reduction in grain size (∼50%) was achieved upon adding 1 wt.% Sm. An equiaxed structure was induced due to modification effect by Sm effect on retarding the recalescence temperature.
3. After Sm additions for Al-4Mg alloy, the solidification reaction temperatures of the precipitation of Mg$_2$Si particles and for formation of a complex eutectic (Al$_3$Fe, Mg$_2$Si, Al$_8$Mg$_5$ and Al) were reduced by 15 °C–20 °C.

![Image](image_url)

**Figure 8.** X-ray images of Fe, Mg, Si, Al, Zr, Ti (a)–(f) corresponding to backscattered image (CP) taken from Al-4Mg-0.2Zr alloy, the AlMgFeZrTi rich intermetallic phase particle observed.

![Image](image_url)

**Figure 9.** X-ray images of Fe, Mg, Si, Al, Zr, Ti (a)–(f) corresponding to backscattered image (CP) taken from Al-4Mg-0.5Zr alloy, the AlMgFeZrTi rich intermetallic phase particle observed.
Figure 10. SEM micrograph taken from Al-4Mg-0.5Sm alloy showing intermetallic precipitations, (a) SEM micrograph, (b)–(d) EDS spectra of points A, B and C in (a), where the precipitations of $\text{Al}_{18.77}\text{Mg}_{1.64}\text{Sm}_{0.02}$ (point A) and $\text{Al}_{19.4}\text{Mg}_{1.57}\text{Sm}_{0.82}$ (point B) intermetallics, the matrix analysis $\text{Al}_{20.1}\text{Mg}_{0.03}\text{Sm}_{0.008}$ (point C).

Figure 11. SEM micrograph taken from Al-4Mg-1Sm alloy showing intermetallic precipitations, (a) SEM micrograph, (b)–(d) EDS spectra of points A, C and D in (a), where the matrix analysis $\text{Al}_{20.41}\text{Mg}$ (point A), the precipitations of $\text{Al}_{25.28}\text{Mg}_{2.77}\text{Sm}_{1.48}$ (point B—not presented), $\text{AlMgSi}_{0.65}$ (point C) and $\text{Al}_{23.42}\text{Mg}_{1.34}\text{Sm}_{0.71}\text{Si}_{0.05}$ (point d) intermetallics.
Rich-intermetallic compounds i.e. agglomerates Al$_{38.76}$Mg$_{7.04}$Ti$_{0.52}$Fe$_{0.07}$ and Chinese script shapes of Al$_{25.28}$Mg$_{2.77}$Sm$_{1.48}$ were detected in microstructure due to Sm or Zr additions.

Figure 12. X-ray images of Fe, Mg, Si, Al, Sm, Ti (a)–(f) corresponding to backscattered image (CP) taken from Al-4Mg-0.5Sm alloy, the AlMgFeSm rich intermetallic phase particle observed.

Figure 13. X-ray images of Fe, Mg, Si, Al, Sm, Ti (a)–(f) corresponding to backscattered image (CP) taken from Al-4Mg-1Sm alloy, the AlMgSiFeSm rich intermetallic phase particle observed.

4. Rich-intermetallic compounds i.e. agglomerates Al$_{38.76}$Mg$_{7.04}$Ti$_{0.52}$Fe$_{0.07}$ and Chinese script shapes of Al$_{25.28}$Mg$_{2.77}$Sm$_{1.48}$ were detected in microstructure due to Sm or Zr additions.
Figure 14. Optical micrograph at magnification 50X which were taken for: (a) Al-4Mg base alloy, (b) base + low Zr, (c) base + high Zr, (d) base + low Sm, (e) base + high Sm.

Table 3. Grain size characteristics according to adding level of Zr/Sm to Al-4Mg base alloy.

| Code               | A (μm²)       | L (μm)       |
|--------------------|---------------|--------------|
| Base               | 135.73 ± 43.58 | 210.41 ± 67.77 |
| Base + Low Zr      | 107.64 ± 40.88 | 165.84 ± 63.23 |
| Base + High Zr     | 92.58 ± 34.33  | 143.56 ± 53.46 |
| Base + Low Sm      | 85.88 ± 25.67  | 132.20 ± 39.69 |
| Base + High Sm     | 72.23 ± 20.99  | 111.09 ± 32.46 |

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Conflicts of interest

The authors declare no conflict of interest.
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