The Effect of Zn on the Properties of Mg-10Al-6Ca-1Sn Alloy

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Abstract. In this study, Mg-10Al-6Ca-1Sn and Mg-17Al-4Zn-3Ca-1Sn composite alloys were prepared. They were prepared by melting them in argon atmosphere on a water-cooled copper hearth. The sample were then analysed to determine the microstructure and mechanical properties using scanning electron microscope (SEM) and hardness testing, respectively. Moreover, a few of tests had been done to observe and determine microstructure and mechanical properties of the alloys. Mg-17Al-4Zn-3Ca-1Sn alloy, the microstructure of Mg-17Al-4Zn-3Ca-1Sn alloy distinctly portrays fine grains, resulting abundant of grain boundaries, which consist of eutectic phase, surround of primary magnesium grains. In contrast, the Mg-10Al-6Ca-1Sn alloy exhibits large differences in grain size. As a control, the sample without the addition of Zn element portrays large particles and creating very small amount of grain boundaries in the captured area of 30 µm. In perspective of mechanical properties, Mg-17Al-4Zn-3Ca-1Sn composite alloy showed higher Vickers hardness value with average of 81.8 Hv compared to Mg-10Al-6Ca-1Sn composite alloy, which was 70.5 Hv. In conclusion, the addition of Zn has effectively improved the hardness of the Mg alloy. This is supported by XRD analysis, which confirms the phase of new alloys that composed of Zinc element.

1. Introduction
Magnesium (Mg) based alloys are becoming some major industrial materials for today’s advancement technology and latest manufacturing application. These alloys are favourable, as it possesses superior properties. With outstanding combination characteristics of high elastic modulus, good damping behaviour, very light in weight and low density, Mg alloys stand as one of the most crucial lightweight materials in structural application [1]. Besides, Mg alloys are often used in motor vehicles and aircraft application including crankcase, tuck coves and gearbox housing [2]. Mg alloys are essential to be developed and improved in order to achieve great performance of alloy with excellent workability.

For instance, it is very lightweight compared to aluminium (Al) and steels. Engineers and scientist have showed so much interest of Mg alloys for decades due to these properties. Study of Mg alloys lead to reasonable prices and properties enhancement of Mg and its alloys will lead to great use of magnesium. This is because compared to using alternative materials, Mg alloys results in a 22% to 70% weight reduction. To add their competitive edge, Mg alloy started to be used in racing cars. Fuel efficiency, increase sustainability and performance are the most important issues. Mg possess low melting temperature (Tm = 650 °C) and hexagonal crystal structure (HCP). Inadequate slip system causes it to soften and weak when being exposed to high surrounding temperature. Alloying helps the materials having good room temperature strength. New composition of Mg alloys with addition of element have been developed. Most frequently used alloying elements are zinc (Zn) and calcium (Ca). Zn will increase the strength of the material at high temperature exposure because of precipitation hardening. Addition of Ca in Mg and Al will act as grain refiner [3]. By alloying, Mg properties may be improving not only...
at high temperature but also in ambient state. In this study, microstructural and hardness properties on Mg-10Al-6Ca-1Sn and Mg-17Al-4Zn-3Ca-1Sn are carried out. The characterization will be carried out by X-ray Diffraction (XRD) technique, Vickers Hardness Testing and Scanning Electron Microscopes (SEM).

Mg alloys are light in weight and own superior damping capacity. However, [4], stated that the low strength and ductility of Mg alloys to Al alloys have limited their application and the higher demands in advance application requires better mechanical properties. Besides, [5] highlighted that Mg-Al suffers poor mechanical properties due to instability of ß (Mg17Al12) phase at elevated temperatures thus limit the application of this alloy. Even though those elements added in are to improve mechanical properties of the alloy, not all properties are developed and some bad side effects can also be seen from the combination made. Al has large affinity towards micro porosity while Ca has low protection towards oxidation process especially in its molten condition, [6], stated that Ca is one of the important elements in Mg alloy as it could improve the ignition-proof of pure Mg. However, the study of Ca addition into Mg alloy of Mg-10Al-6Ca-1Sn and Mg-17Al-4Zn-3Ca-1Sn have not been studied. Moreover, [7] stated that Mg2Sn alloy superior heat resistance properties can fix the weakness of Mg that tends to soften easily at elevated temperature. Therefore, it is interesting to study the effect of Zn and Ca addition into Mg alloy.

[8] stated that increasing strength of Mg alloys at high or room temperature are based on Mg and Al with additional combination of Zn, Ca, Si and radical earth (RE). The ternary element Zn is added to the binary alloy to develop the response process of precipitation hardening [9]. This is because Zn is almost three times stronger than Al as it possesses better solid solution strengthening properties especially after being treated and under quenched state. [10] highlighted that fracture toughness of pure Mg was low which reported to be only 17.8 MPa m1/2. However, in Mg-1.6 at.% Zn solid solution strengthening, the value rise by 5.9 MPa m1/2 to 23.7 MPa m1/2.

Sn is beneficial in alloying when it is combined with Mg and small amount of Al by substituting into few metallic phases [11]. In this study, 1 wt.% of Sn is added to improve properties of Mg alloys. Previously, [12] highlighted that (1-10) % of Sn can improve the creep resistance in Mg alloy. They added that Sn content helps in refining secondary dendritic arm spacing of the primary α-Mg phase. The precipitation of Mg2Sn results in increment of compressive and tensile strength by which affected to finer grain refinement of Mg alloys [12]; [13]. Addition of Sn into Mg alloys will increase the strength of the materials and improve the ductility. By the addition of Sn, yield strength and hardness will increase due to intermetallic phases. Grain refinement and solid solution strengthening of Mg-Sn give strengthening effect in single-phase alloy where this will result in better mechanical properties to Mg alloys.

By the addition of Sn, it is expected to give superior properties to the alloy. However, Sn element is quite expensive which can cause increasing of the production cost. Hence, over addition of Sn in the alloy can bring limitation in cost aspect to the production too. New findings of Mg alloys are very crucial in order to develop the materials to have close tolerance towards requirement for commercial purposes. In this study, Mg-10Al-6Ca-1Sn and Mg-17Al-4Zn-3Ca-1Sn samples were carried out so that Mg alloy mechanical properties can be improved. It is expected to obtain better microstructure, good damping behaviour, increment of hardness and elastic modulus in Mg alloys by the addition of few elements like Sn, Al, Ca and Zn. Good mechanical properties and high strength will result in high durability and long-life span of the products. Improvement of Mg alloy can bring enhancement in the latest technology production while at the same time widened the field of Mg studies

2. Materials and Methods

2.1 Sample Preparation
Mg-10Al-6Ca-1Sn and Mg-17Al-4Zn-3Ca-1Sn composites were prepared using 99.5% Mg, 70 % Mg-30 % Ca master alloy ingot, Sn ingot, Zn chips and Al shots. The samples were measured and weight accordingly, then melted using an arc-melting furnace in argon atmosphere on a water-cooled copper hearth. Then sample were placed inside the furnace. The chamber were vacuumed for at least five minutes and argon gas were flushed into the chamber. This process were done twice to ensure the
chamber atmosphere is filled with argon gas. Airflow need to be in control to avoid sample was blown away due to high speed of airflow and the tightly closed door of the furnace to avoid air from diffusing into the chamber and causing the sample to oxidize. Once purging completed, titanium (Ti) getter and the samples were then be melted in order to eliminate impurity gases such as oxygen and nitrogen. Once completed, melting process will continue by melting of the samples. Samples were be mounted using cold mounting epoxy and hardener according the ratio of 9:1. The mixture of epoxy and hardener were transferred into a polystyrene cup and stirred slowly. The samples were left for 4-5 hours in order to let it harden. The mounting which the specimen is embedded in the solution/solvent have purposes to ease in handling and protect the specimen physically.

After the mounting processes, the specimen were grounded using silicon carbide abrasive paper. Figure 1 shows Metkon Gripo 2V Grinder-Polisher that used in this process. The purposes of this step is to eliminate the damage from cutting, remove contaminants and also repair the surface of the specimen. The grinding processes starts from 120, 240, 600, 800, 1000 and 1200 grit consequently. Proper grinding can help minimizing time spending for polishing process. For polishing process, polishing cloths and diamond slurry were used to gain a better surface finish that possess high reflectivity before any microscopic testing can be done. Diamond slurry were used as it offers highest level of accuracy that can either be water-based or oil-based slurries. In this experiment, water-based slurry, which is harmless to the environment with super cleaning properties, were used to polish the metallic specimen.

![Figure 1. Grinder Polisher (Metkon Gripo 2V)](image)

After grinding and polishing, the samples were be etched by strong acid to remove the surface of the exposed area in order to achieve a better microscopic view. Etching is done in order to remove oxide layer that might form at the surface area or any impurities adhered onto it. The etchants help to cut the unnecessary parts and reveal the protected parts. Etching is done by immersing sample into the strong acid and is left for a moment in range 3-60 seconds. The etchants than can be used for Mg alloys is glycol solution.

### 2.2 Mechanical Characterization

For mechanical behaviour of the specimen finding, hardness testing were conducted by vickers hardness tester, Shimadzu HMZ Series. By using load of 500g and dwell of 15 seconds, a square based pyramid shape were used to lift the load. An indenter having an angle of 136° must sufficiently harder than the specimen tested so that it cannot easily deformed by the force applied.

Once the testing over, the width or depth of the indentation were measured to determine the hardness of the sample tested. The vickers hardness is the quotient of the tested load applied (500g) for the area of the indentation in millimetre, mm unit by considering the upside down square base pyramid. vickers hardness is identified according to equation (1) and (2):

\[
HV = \frac{2F \sin 136^\circ}{d^2}
\]  

(1)
\[ HV = 1.854 \frac{F}{d^2} \]

where; \( F = \text{load} \) (kgf), and \( D = \text{average value of two diagonals, } d_1 \text{ and } d_2 \) (mm)

2.3 Microstructural and Phase Analysis
Microstructural examination of samples was conducted by using SEM, INCA, SUPRA 40V 40VP) Zeiss. It was used in order to observe the microstructure of that composites. The standard grinding and polishing method were used to prepare the sample for SEM observation. The sample were grind using silicon carbide paper from 120 grit to 1200 grit and then followed by polishing process that use diamond slurry from 6 μm to 1 μm. The formation of new phases in this work was monitored by Shimadzu X-ray diffraction XRD-600 with Cu-K\( \alpha \) radiation operated at 30 kV and 20 mA and 20 between 20 to 100 °C at the scanning rate of 2°/ min.

3. Results and discussion
3.1 Hardness Testing
The vickers hardness test was performed to measure the micro hardness of the two different alloys at least three different regions were indented for each sample under a load of 0.4 kg for 15 seconds time dwelling. Mg-17Al-4Zn-3Ca-1Sn composite alloy shows a higher Vickers hardness value with average of 81.8 H\text{v}. Meanwhile, Mg-10Al-6Ca-1Sn composite alloy exhibits 70.5 H\text{v}. It is hypothesised that Alloy with the addition of element Zn is predicted to have higher vickers hardness than the one without Zinc. Zn is approximately three times affective on an atomic per cent basis than aluminium in the yield strength for alloys. It is shown that Mg-4Zn-6Ca-1Sn alloy has higher resistance to the localization of plastic deformation compared to Mg-10Al-6Ca-1Sn alloy. Figure 2 shows the Vickers hardness value both of Mg-10Al-6Ca-1Sn and Mg-17Al-4Zn-3Ca-1Sn composite alloys. [14] found that studied by adding Zn as the alloying element into Mg-based composite, the microhardness value has increased about 12%, suggesting that zinc shows a greater effect on the hardness value. In another work by [15], the Mg alloy portrays higher hardness value when the Zn contents increased. This is due to the intermetallic components and formation of precipitate in the alloy.

![Figure 2](image_url)

**Figure 2.** Vickers hardness value both of Mg-10Al-6Ca-1Sn and Mg-17Al-4Zn-3Ca-1Sn alloys

3.2 Microstructure
Microstructural analysis was perform at the magnification of 2000x for both samples in size of 30µm. Based on the morphological in Figure 2, there are two different types of eutectic morphology in both two samples. Mg-17Al-4Zn-3Ca-1Sn, was found to have one with brighter white contrast, which involves lamellar phase richer in terms of Mg-Ca-Zn. On the other hand, the lamellae of the second
eutectic with the grey contrast was determined as a phase richer in other elements like Mg-Al-Ca-Sn. Meanwhile, in Mg-10Al-6Ca-1Sn, the Mg-Ca exists in lamellar phase with brighter white contrast and the remaining elements in the grey contrast. [16] stated that the eutectic is a common pattern when it comes to Mg – Al alloy and Zn addition is related to the changes of the phases in the alloy.

For Mg-17Al-4Zn-3Ca-1Sn alloy, the microstructure distinctly portrays fine grains and therefore resulting abundant of grain boundaries, which consist of eutectic phase, surround of primary magnesium grains. In contrast, alloy sample of Mg-10Al-6Ca-1Sn alloy shows large differences in grain size. With the same magnification, the alloy without addition of Zn element tends to have large particles and creating very small amount of grain boundaries in the area of 30µm captured. This is due to the group of alloys that present based mainly on the Mg-Al system, which tends to have large and variable grain size. The addition of Zn to Mg metal alloys has increased the amount and continuity of the compound at the grain boundaries [11]. Zn acts as grain refiner that attributed to inoculation of the particles in the alloy. The presence of Zn atoms has contributed to the solid solution strengthening, as the presence of grain boundary phases reduces grain boundary sliding [3]. Therefore, an easiest way to improve the strength of a material is to make grain small as possible, increasing the amount of grain boundary. Smaller grains have greater ratios of surface area to volume, which result in greater ratio of grain boundary to dislocation.

![Figure 3](image1.png) ![Figure 3](image2.png)

**Figure 3.** Microstructure of (a) Mg-10Al-6Ca-1Sn and (b) Mg-17Al-4Zn-3Ca-1Sn observed by SEM with 2000x magnification

### 3.3 X-ray diffraction

Figures 4(a) and (b) show the XRD pattern of Mg alloys without and with the presence of Zn metals, respectively. Coherent scattering by diffraction of x-ray can detect crystal structure of materials shows the two XRD pattern are polycrystalline with sharp peaks in each graph. We found that patterns correspond to the peaks of Mg alloys with and without Zn element as Mg-17Al-4Zn-3Ca-1Sn has more peaks than Mg-10Al-6Ca-1Sn alloy. As Mg composition is the highest in both alloys, it also shows the highest peak in XRD pattern. Furthermore, the lower intensity peaks of Zn and Sn elements is lower compared to Mg, Al and Ca. This is due to small percentage of the elements content added into the alloy.

The Mg peak was detected in all samples. From XRD pattern the results shown that the addition of 4 wt% of Zn does not lead to the production of intermetallic phase. [16] stated that some intermetallic phase will form if the Zn composition reach in ranging of 29 wt% to 53 wt%. Intermetallic phases such as Mg$_2$Zn$_{11}$ and MgO were detected and existed in Mg-17Al-4Zn-3Ca-1Sn composite alloy.
Figure 4. XRD pattern of (a) Mg 10Al-6Ca-1Sn and (b) Mg-17Al-4Zn-3Ca-1Sn composite alloys

4. Conclusions
We conclude that:

i. Mg-17Al-4Zn-3Ca-1Sn composite alloy exhibits higher hardness value compared to Mg-10Al-6Ca-1Sn. This is due to the addition of Zn element that has induced the formation of finer grains within the alloys.

ii. Intermetallic phases such as Mg$_2$Zn$_{11}$ and MgO were found in the Mg-17Al-4Zn-3Ca-1Sn composite alloy, which confirmed by XRD.

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