Effects of Ca Addition on Microstructure and Hot Deformation of AZ61 Magnesium Alloy

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Abstract. Magnesium and its alloys are potential candidates in the transportation sector being the lightest structural material. In this work, effects of calcium addition in as-cast and homogenised AZ61 (aluminium 6 wt.% and zinc 1 wt.%) magnesium alloy was investigated. Phase prediction based on thermodynamic data indicated that formation of Al$_2$Ca phase could effectively suppress the formation of Mg$_{17}$Al$_{12}$ phase. This Al$_2$Ca phase was present in the microstructure in almost the actual stoichiometry, as found in SEM EDS. The formation of this phase was also confirmed by DSC. During hot compression, recrystallization took place irrespective of temperature. However, at elevated temperature, slight grain growth of the refined grains was evident. This was due to the thermal energy from the test temperature. Nevertheless, such grain growth was not very effective due to the presence of nano-size Al$_2$Ca phase, which provided pinning effect by positioning at the grain boundaries.

1. Introduction
Magnesium (Mg) is one of the lightest structural materials with low density (1.74 g/cm$^3$) as well as high specific strength. Magnesium alloys generally indicate weight reduction which results in reduction in fuel and energy consumption [1]. As they inherit low density, high specific strength, good thermal and electrical conductivities, they have been used for a wide variety of applications [2-4]. Magnesium alloys improve fuel efficiency of vehicles and reduce CO$_2$ emission due to their high specific strength and stiffness which have been a great fallback for steel and aluminium alloys in the transportation industries [3, 5-7]. They can be a considerable substitution of plastics in the field of electronic and computer industries as well [8]. In spite of these promising properties, most magnesium alloys have low formability which limits their uses in the automotive and aerospace sectors.

The addition of calcium (Ca) Mg-Al-Zn alloys generally guides to the formation Al$_2$Ca (Melting Temperature-1352 k) [9]. In case of AZ31 alloy, the strength and creep properties can be improved through particle strengthening due to the presence of this hard and thermally stable Al$_2$Ca phase [10]. When the microstructure was refined by thermomechanical processing (extrusion, rolling etc.), a surpassing superplasticity is revealed by the calcium containing AZ31 alloy in comparison with the bare AZ31 alloy. This unique characteristic is unveiled due to the effective pinning effect of Al$_2$Ca particles that impedes grain coarsening during the high temperature deformation [11-13].

In this current work, effect of Ca addition in AZ61 magnesium alloy was investigated during hot deformation to determine temperature and strain rate dependency on deformation. Thermodynamic modelling was carried out to understand the dominating phases at different temperatures.
2. Experimental
The experiments were conducted by using AZ61 alloy which contains 6% Al, 1% Zn, 2% Ca. It was prepared by melting in an induction furnace in a mild steel mould in presence of Ar gas flow after being preheated at 300°C. After casting, a rectangular bar was produced having a dimension of 30 cm in length, 14 cm in width 15 mm in thickness. The bar was carefully cooled in air after casting. Then after machining, four rectangular bars having thickness of 12 mm from the initially produced cast bar.

X-ray Fluorescence (XRF) was conducted as well to detect the abundances of elements that are present in the cast samples. Homogenization treatment was carried out at 420°C for 18 hours followed by water quenching. The hot compression specimens had cylindrical height of 15 mm and diameter of 10 mm. After sample preparation, hot compression tests were conducted in a Testometric UTM machine (M500-50CT) at four distinct temperatures—300 °C, 350 °C, 400 °C and 450 °C. Specimens were heated up to the test temperature and maintained at that temperature for 30 min prior to hot compression. The specimens were lubricated with graphite to reduce friction at the punch-specimen interface. The initial height of the test specimens were reduced to 75% at two separate true strains: i) $\varepsilon_1=0.125$, ii) $\varepsilon_2=0.063$. Then the specimens were air cooled and the deformed lengths were measured.

For microstructure analysis, standard sample preparation techniques were applied to the deformed specimens followed by etching in acetic picral. Images were acquired in an optical microscope OPTIKA B-600MET equipped with an image analyser for microstructure examination. Scanning electron microscopy (SEM) equipped with Energy-Dispersive Spectrometer (EDS) was carried out by JSM-7640F field emission scanning electron microscope. SEM characterisation with optimum resolution at optimum depth of field was applied for observing second phase particles. The quantitative analysis of the chemical composition of the phases in the homogenised alloy was performed using EDS in back-scattered electron mode.

Differential scanning calorimetry (DSC) was performed on the as-cast sample (27 gm) to measure temperature difference in various phase transitions. For this test, starting and finishing temperatures were room temperature and 550 °C respectively with a heating rate of 5 °C/min.

3. Results and Discussion
3.1 Microstructure of the Alloy
The chemical composition of the alloy is given in Table 1. In the initial calculations, the amounts of alloying elements were fixed at Al 6 wt.%, Zn 1 wt.% and Ca 2 wt.%.

| Element | Wt% |
|---------|-----|
| Mg      | 90.75 |
| Al      | 5.99 |
| Ca      | 2.19 |
| Zn      | 1.05 |
| Fe      | 0.03 |

Optical micrographs of the alloy are shown in Figure 1 in as-cast and homogenised conditions. The extent of coring is evident in the as-cast microstructure. Dendrites of the matrix $\alpha$ phase is also clearly visible. After homogenisation, the amount of coring is reduced and the microstructure is more uniform.
3.2 DSC Analysis

Figure 2 shows DSC analysis of AZ61-Ca alloy. The sample shows an endothermic peak at 532.5°C. The temperature indicates the characteristic property of the sample. At this temperature phase changing reaction occurs. Since DSC is carried out up to 600 °C, complete melting of the alloy is not represented in the curves. The peak obtained at approximately 532 °C is explained in the following section.

3.3 Effects of Ca on Phase Formation

In AZ61 alloy, the amount of Zn is approximately 1%. This little amount of Zn is completely dissolved in α-Mg matrix. In this context, Zn is totally present in the α-Mg matrix and does not form any considerable individual phase.

Thermodynamic modelling calculations were carried out for 700 to 200 °C. Generally, it is considered that Scheil-Gulliver solidification model provides a better prediction of the solidification condition. However, 18 hours of homogenisation at 420 °C is considered to be adequate to bring the system towards equilibrium and hence, phase predictions were made under the equilibrium condition. In Figure 3, calculations were made for the same alloy system with and without Ca addition and room temperature was considered as the phases present at 200 °C. This is due to inaccuracy of the predictions at lower temperatures. Without Ca addition, solidification started at 604.36 °C and completed at 509.42 °C. When Ca was added to the system, these temperatures were altered slightly. Solidification started at 615.7 °C and completed at 501.48 °C.
Predicted phases are $\text{Al}_2\text{Fe}$, $\text{Al}_5\text{Fe}_2$, $\text{Al}_3\text{Fe}$, $\text{Mg}_{17}\text{Al}_{12}$, $\text{Al}_2\text{Ca}$ and $\text{Al}_2\text{Ca}$. Amongst these phases, a few Fe containing phases are less than 0.10%. These are omitted from discussion as their stability may not be accurate.

According to the prediction, the characteristic $\text{Al}_2\text{Ca}$ phase started to form at approximately 530 °C. This is in close-match with the experimental results of DSC.

The calculated area fraction of the $\beta\text{Mg}_{17}\text{Al}_{12}$ was 4.6 wt.% and $\text{Al}_2\text{Ca}$ (denoted by $\text{Al}_2\text{Re}$) was 5.14 %. Surprisingly 2% Ca has a profound impact on the stability of $\beta$ phase. Without Ca, the phase content was approximately 8.44%. It implies that Al has more affinity towards Ca to form $\text{Al}_2\text{Ca}$ phase. Generally, addition of Ca to the AZ61 alloy leads to the formation of $\text{Al}_2\text{Ca}$ or $\text{Al}_2\text{Ca}$ phase with a decrease in the amount $\beta\text{Mg}_{17}\text{Al}_{12}$.

When Ca is added, it leads to the formation of $\text{Al}_2\text{Ca}$ or $\text{Mg}_2\text{Ca}$ intermetallics. As the electronegativity difference between Ca and Al ($\Delta\text{EN}=0.61$) is higher than that of Ca and Mg ($\Delta\text{EN}=0.31$), $\text{Al}_2\text{Ca}$ is likely to form in this circumstances [14]. The formation of $\text{Mg}_2\text{Ca}$ phase can be obtained due to the presence higher amount Mg (background pickup during EDS). Figures 4(a), 4(b), 4(f) contains large amounts of Mg and Ca. As the amount of Al is much lower, $\text{Mg}_2\text{Ca}$ phase is formed rather than $\text{Al}_2\text{Ca}$ phase (Table 2). However, from Figures 4(c), 4(d) and 4(e), it is evident that there is considerable amount of Ca and Al. So, $\text{Al}_2\text{Ca}$ phase is formed in this situation due to the electronegativity effect (Table 2).

Owing to these circumstances, Al tends to react with Ca rather than Mg. With the increase of Ca content, the amount of $\text{Al}_2\text{Ca}$ precipitates increases which concludes the reduction of the available Al content in the alloy during solidification. This incident sums up with the reduction in the $\beta\text{Mg}_{17}\text{Al}_{12}$.

From further observation in SEM, some small particles were observed which were embedded on the matrix (Figures 5(a), 5(b) and 5(c)). In Figure 5(a), $\text{Al}_2\text{Ca}$ particles are clearly seen to be present both at grain boundaries and in grain interior. The particle sizes also vary. Particles of micron sizes are present. Moreover, nano-size $\text{Al}_2\text{Ca}$ of sizes less than 100 nm were also vividly embedded in the matrix. These embedded particles consist of $\text{Al}_2\text{Ca}$ phase. They impede grain growth due to the Zener pinning effect.

![Figure 3. Equilibrium Model of AZ61 alloy with and without 2% Ca addition](image-url)
Figure 4. Particle present in the microstructure of the AZ61-Ca alloy

Table 2: The EDS analysis result on the SEM images in Figure 4

| Figure | Mg (at.%) | Al (at.%) | Ca (at.%) | Zn (at.%) | Phase  |
|--------|-----------|-----------|-----------|-----------|--------|
| a      | 94.16     | 1.77      | 3.67      | 0.40      | Mg2Ca  |
| b      | 91.28     | 1.72      | 6.28      | 0.72      | Mg2Ca  |
| c      | 50.02     | 8.38      | 40.67     | 0.92      | Al2Ca  |
| d      | 64.13     | 15.11     | 19.36     | 1.41      | Al2Ca  |
| e      | 68.23     | 22.46     | 8.87      | 0.44      | Al2Ca  |
| f      | 92.68     | 2.05      | 4.61      | 0.66      | Mg2Ca  |

3.4 Stress-Strain Curves during Hot Compression

The flow curves are shown in Figure 6. The curves represent typical dynamic recrystallization behaviour. At the initial stage, the flow stress increases up to a maximum stress due to strain hardening by continuous accumulation of dislocations and an increase in dislocation density. Afterwards the stress decreases with increasing compressive strain. Such softening behaviour is observed due to dynamic recrystallization and nucleation and coarsening of β particles after a critical strain [15–17]. Such behaviour is attributed to both temperature and strain rate.

Figure 5. Embedded particle on the matrix (a) 500x (b) 37000x (c) 160000x

At low temperatures as well as at high strain rates, hardening followed by softening is more promising, whereas at high temperatures and low strain rates, a dynamic equilibrium between hardening and softening occurs at the very beginning of deformation. At high strain rates, dislocation multiplication is more rapid than at low strain rates and contributes to higher strain hardening effect. Figure 6 shows such steady stress continues more in case of 0.125 s⁻¹ strain rate than that for 0.063 s⁻¹ strain rate for a certain strain range. This is as well noticeable that after the steady stress, flow stress increases with increasing strain due to hindrance in deformation by increase in the size of recrystallized grains and
their area fraction decreases by increasing test temperature. Such behaviour is more prominent at low strain rate and begins at lower testing temperature.

![Figure 6](image)

**Figure 6.** Compression curves for the homogenised specimens. (a) At a strain rate of 0.063 s$^{-1}$ and various temperatures; (b) At a strain rate of 0.125 s$^{-1}$ and various temperatures

### 3.5 Microstructural Changes during Hot Compression

Figure 7 shows the evolution of microstructure at strain rates of 0.063 and 0.125 s$^{-1}$ for various temperatures. Comparing with the as-cast and homogenised microstructures (Figure 1), the grains are much smaller, indicating refinement of grains. With increasing temperature, grain growth had occurred to some extent. However, due to the presence of Al$_2$Ca phase, such growth is not substantial. Nano-sized particles of this phase is believed to effectively block grain growth even at elevated temperature due to pinning effect.

At 300 °C, the grains are broken, elongated and grain distribution is heterogeneous. The microstructure is more dendritic type at lower temperatures and higher strain rate. Dendritic type microstructure changes to planar type as temperature and strain is increased. As gradients near the grain boundary provides suitable site for nucleation, so recrystallization occurs at higher temperatures. At a constant strain, the average grain size increases with increasing the deformation temperature due to the increase in the restoration rate [15]. Grain refinement occurs at high temperatures (e.g. 450 °C). Refinement of grains and growth is more prominent at the higher strain rate. After refinement grains are homogeneous. Ca addition to the AZ61 alloy causes effective refinement to the microstructure of the alloy. From the SEM analysis, Figure 5 indicates that Al$_2$Ca is extensively present in the alloy. As testing temperature is increased, the size of recrystallized grains increases and their volume fraction decreases. Therefore, finer grains can be gained by increasing strain without increasing too much temperatures.
Figure 7. Optical microstructure evolution of AZ61 with 2% Ca addition during hot compression tests at ε=0.063 and temperatures of (a) 350 °C, (b) 400 °C and, (c) 450 °C and tests at ε=0.125 and temperatures of (d) 350 °C, (e) 400 °C and, (f) 450 °C

4. Conclusions
In this work, effects of Ca addition in AZ61 alloy was investigated during hot compression.
- Addition of calcium led to the formation of \( \text{Al}_2\text{Ca} \) phase. This phase has effectively suppressed the stability of \( \text{Mg}_{17}\text{Al}_{12} \) phase.
- DSC curves correlates well with the predicted results of phase formation from thermodynamic simulation.
- \( \text{Al}_2\text{Ca} \) phase is present in the microstructure in stoichiometric composition of slight variation. SEM results confirmed that the phase can be present in different sizes—particles of size less than 100 nm was also detected.
- During hot compression, recrystallization has occurred intensely, irrespective of temperature. However, grain growth was evident at elevated temperatures. As expected, higher temperature was responsible for grain growth. Nonetheless, grain growth did not occur profoundly due to the presence of nano-size particles.
- Higher deformation rate is beneficial for formation of refined grains.

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