

Combined effect of calcium addition and ageing treatment on Mg-6Al-1Zn-XCa alloy immersed in 3.5wt. % NaCl solutions

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Abstract

The effect of aging at different temperatures of 180°C, 200°C, 220°C, and 240°C with various levels of calcium (X=0.5, 1.0, 1.5, 2.0 wt.%) addition of Mg-6Al-1Zn-XCa alloy was investigated in 3.5wt. % NaCl solution. The specimen was subjected to immersion testing in 3.5wt.% NaCl and the resulted surface were analysed to study the corrosion behaviour and its surface topography by optical microscopy (OM), scanning electron microscopy (SEM), energy dispersed spectroscopy (EDS) and X-ray diffraction (XRD) techniques. The result shows that corrosion attack occurred predominantly on β -phase and the α -phase exhibit relatively minor corrosion. In addition to that the increased aging temperature coarsens the intermetallic as well as α -Mg grains, which shows adverse effect to corrosion resistances and the best result were obtained at composition of 0.5wt. % Ca aged at 200°C.

Keywords: Calcium; Immersion; Corrosion resistance; X-ray diffraction; Ageing.

Introduction

The need for lightweight materials in various industries, especially in automotive and aerospace applications has shown significant increase due to the advantage of fuel and great energy saving and utilization [25-26], and among the lightweight materials Magnesium alloys are one of these lightweight material, having greater chemical stability, machinability and significant high strength to weight ratio [2]. However, their low level of mechanical properties and poor corrosion resistance in chloride environments limits their wider applications [3]. However, it was found that small addition of Ca to a magnesium alloy shows significant increase its strength and corrosion resistance [4-8] in chloride environments. At present, the most widely used magnesium alloys are AZ series materials and the Corrosion Behaviour of magnesium alloy depends on (i) the composition of the Alpha-Mg matrix, (ii) the composition of the other Phases and (iii) its distribution in the matrix [9-

14]. Immersion testing is one of the simplest and effective method to study the corrosion behaviour, which was used in this study and the testing procedure been followed is compliance with ASTM G1-72 [15-16]. Based on the literatures the properties of PH Mg alloys depend on the precipitates and its distribution in the matrix [17-21]. And this study is focused on understanding the ageing phenomena with different temperatures and the effect of a Ca addition to its corrosion behaviour.

2. Experimental Procedure

2.1. Casting

The melting of pure Mg (93wt. %), Al (6wt. %) and Zn (1wt. %) was carried out in stir casting furnace of capacity 1Kg, once the melt was completely in liquid state, Mg-Ca master alloy was added at 720°C, and leave 0.5Hrs for reaction and stir the pool to make uniform melt, subsequently at 650°C of the melt, the gas mixture of 99 % or +1% SF₆ is passed into the crucible at a flow rate of 0.25m³/hour to prevent the unwanted atmospheric contamination to the mat. Then pour the melt into the pre-heated (250°C) metallic mould. The chemical compositions of the experimental alloys are listed in table 1.

Table 1. Chemical Analysis of experimental alloy (mass fraction, %)

Experiment al alloy	Al	Zn	Ca	Mn	Fe	Cu	Si	Mg
AZ61	5.78	0.923	-	0.14 2	0.0148	0.004	0.060 7	Bal.
AZ61+0.5Ca	5.95	0.887	0.40	0.16 5	0.0099	0.004	0.054 9	Bal.
AZ61+1.0Ca	5.67	0.828	0.8 8	0.17 3	0.0125	0.004	0.051 3	Bal.
AZ61+1.5Ca	5.67	0.828	1.33	0.17 3	0.0125	0.004	0.051 3	Bal.
AZ61+2.0Ca	5.33	0.839	1.92	0.17 2	0.013	0.004	0.050 3	Bal.

2.2. Sample Preparation

The sample for the microstructural analysis, being prepared from the cylindrical shaped casting, mounted and subsequently polished for the microstructural analysis.

2.3. Immersion Testing

The testing is performed as per ASTM G1-72 and the solution (corrosion environment) of 3.5wt.% NaCl was prepared using analytical reagent and distilled water. The specimen shall be immersed completely in

the solution for at least 72 hours continuously maintained at room temperature.

2.4. Evaluation of Corrosion Rate

The corrosion rate was carefully studied by weight loss method as per ASTM G1-72. After the exposure, the specimens were removed from the bath, rinsed with distilled water, dried using compressed air, dried in a desiccator for 1-2 days and weighted to determine the sample weight with corrosion products.[27]

The calculation was performed based on the following formula

$$\Delta W_{cp} = \{(W_{acp} - W_b)[mg]\}/(\text{specimen area } [cm^2]) / (\text{exposure time } [d]) \text{ ---- (1)}$$

Where

ΔW_{cp} -Weight Change rate (with corrosion products)

W_{acp} - Sample weight after the test with corrosion products

W_b - Sample weight before the test

For the Mg alloy corroded specimens, the corrosion products on the surface of the corroded samples were removed by immersing in a chromic acid solution of 200g/L CrO_3 + 10g/L $AgNO_3$ at room temperature for 5-10 min, and then the sample was washed with distilled water, dried with warm compressed air, and further dried in a desiccator for 1-2 days. Then the calculation of corrosion rate was determined using the following formula.

$$\Delta W_m = \{(W_b - W_{am})[mg]\}/(\text{specimen area } [cm^2]) / (\text{exposure time}[d]) \text{ [15-16] ----(2)}$$

Where

ΔW_m -Weight change rate

W_{am} -With no corrosion products

Results and Discussion

3.1. Microstructure Analysis

3.1.1. Effect of Calcium Addition on the Microstructure

The microstructural analysis being performed in optical microscope (DIC Leica, USA).

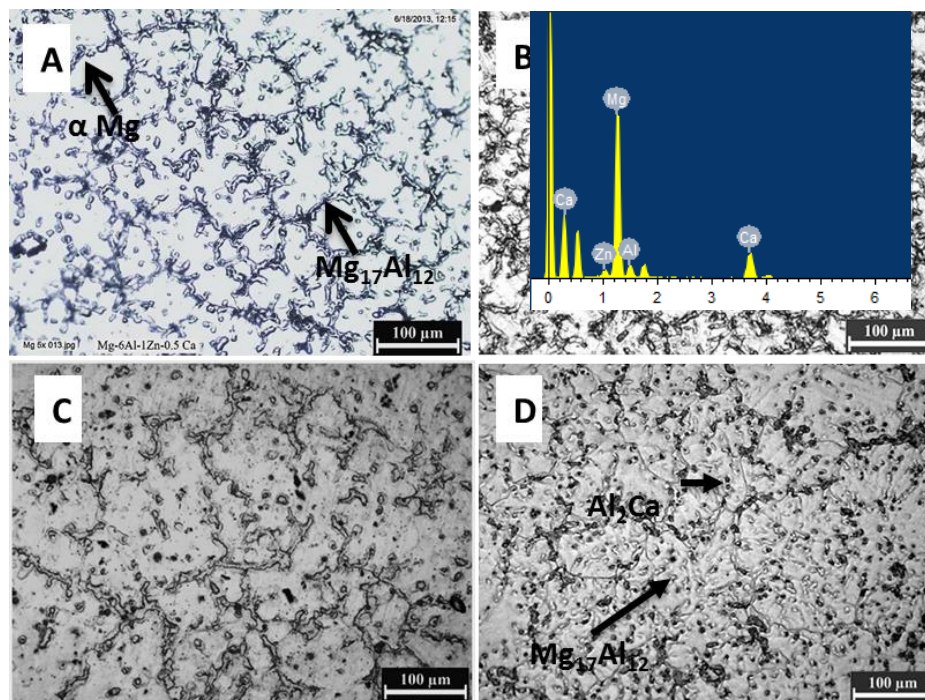
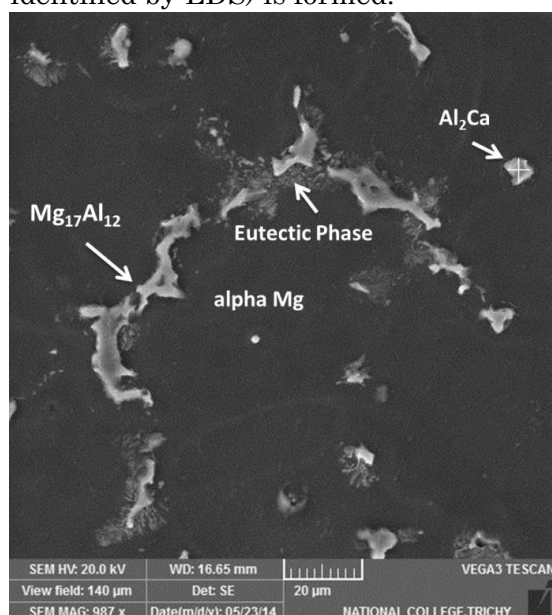


Fig.1. Effect of calcium addition on the Microstructure of alloy AZ61 (a) 0.5% Ca (b) 1.0% Ca (c) 1.5% Ca (d) 2.0% Ca [Etchant 2%Nitol]

Fig.1 shows the effect of Ca addition on the microstructure of AZ61. It is evident that the Ca addition refines α grain size as the, which enhance the mechanical properties [Fig.1]. This phenomenon explains that the addition of Ca generates the heterogeneous nucleation of Al_2Ca and it restricts the growth of α grain size. In addition to that the beta ($\text{Mg}_{17}\text{Al}_{12}$) grain size also decreases with increasing Ca content, which reduces/replaces Al_2Ca intermetallic in the matrix, which lead to improve the corrosion resistance (Fig.2). With the addition of Ca, the $\text{Mg}_{17}\text{Al}_{12}$ -Mg co-operative eutectic has a reduced quantity or disappears and a new Al_2Ca phase (light grey, also identified by EDS) is formed.



Element	Weight %	Atomic %
Mg K	65.95	73.73
Al K	10.53	10.60

Ca K	22.42	15.21
Zn K	1.10	0.46
Totals	100.00	100.00

Fig.2.SEM image of AZ61+ 0.5% wt. of calcium addition

3.1.2. Effect of Aging Temperature on the Microstructure

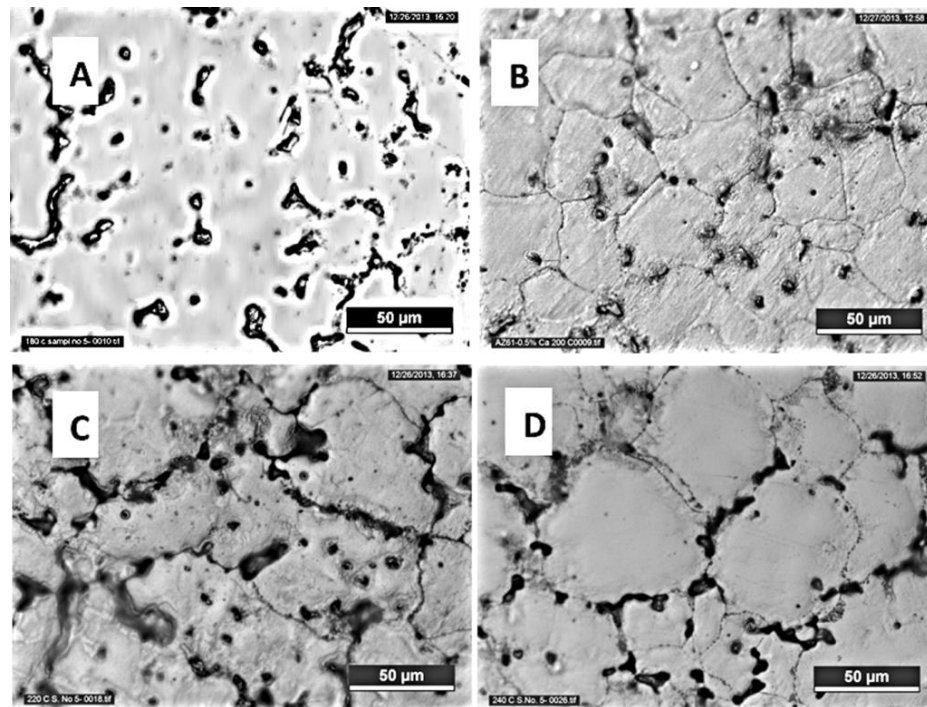


Fig.3.Effect of Aging Temperature on the Microstructure AZ61+0.5Ca addition, aged at 16 hrs. (a) 180° C (b) 200° C (c) 220° C (d) 240° C

All the four combinations listed in Fig. 1. were experimented to study structural changes at different level of aging temperature, and the results shows that, the alloy of AZ61+0. 5Ca gives better results compared to all other alloy combinations, which was presented in Fig 3. And been selected for further investigation. Based on the evaluation of the micrographs presented in Fig 3, (A, B, C, D). The specimen aged at 200°C shows refined grains and fine and uniform distribution of Al₂Ca along the α grain boundary.

3.3. Microstructure at Various Stages of Aging

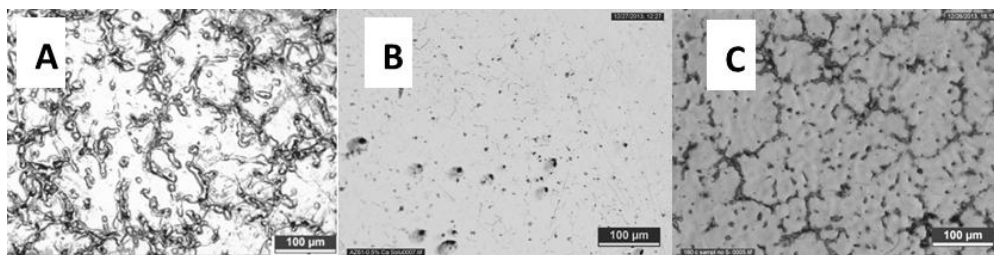


Fig.4. Microstructure of AZ61-0.5Ca-Mg alloy during aging (a) without aging (b) Solutionized at 420°C (c) Aged at 200°C for 16hrs

At Solutionized condition, the micrograph shows the complete dissolution of β ($\text{Mg}_{17}\text{Al}_{12}$) phase, and subsequent ageing for 16 hours followed by air-cooling. The resulted microstructure (Fig 4.c) shows the nucleation of β ($\text{Mg}_{17}\text{Al}_{12}$) which enhances the mechanical properties (Fig.7.) and the heterogeneous nucleation of Al_2Ca intermetallic in the matrix, which significantly improves the corrosion resistance.

3.2. XRD analysis

The X-ray Diffraction (XRD) analysis was performed to identify the phases that formed during the aging process. Fig 5. Shows the, XRD analysis of Base AZ61 material (without Ca addition) and AZ61+0.5wt% of Ca with and without aging. And the result clearly shows that the presence of Al_2Ca in AZ61+0.5wt% of Ca added and aged at 200°C specimen.

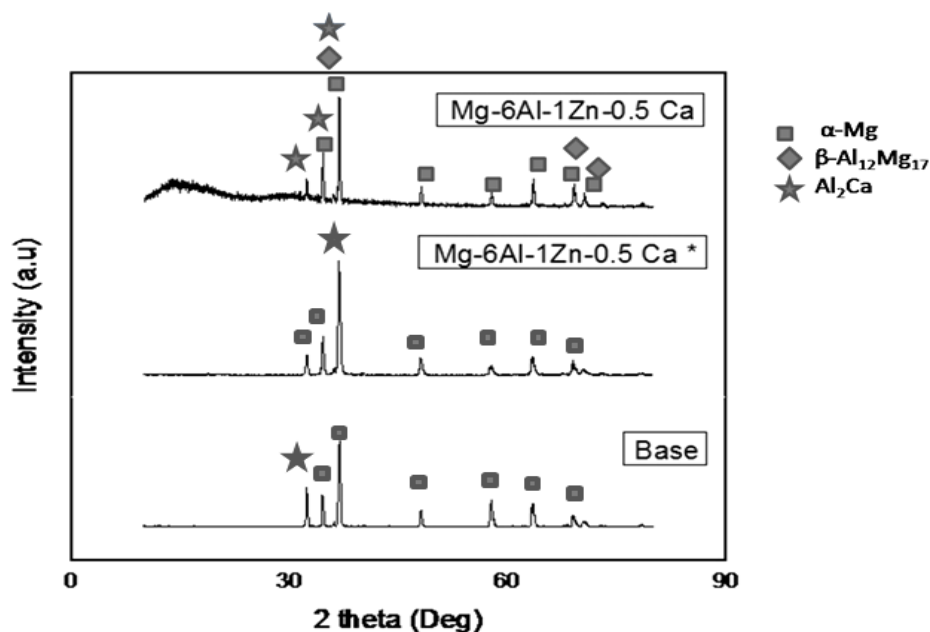


Fig.5.XRD analysis of calcium added samples and AZ61 Base, * indicate specimen without aging.

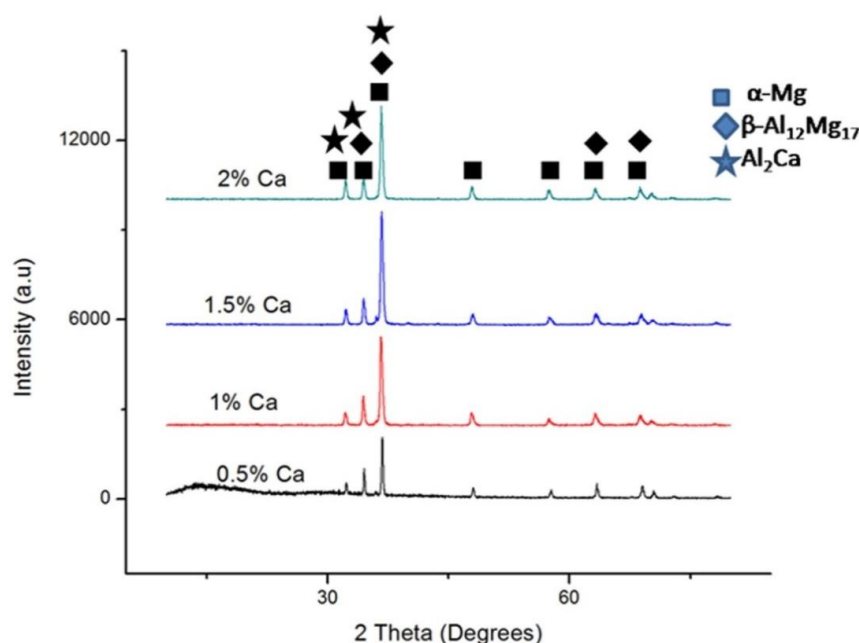


Fig.6.Effect of calcium on the XRD result (a) 0.5% Ca (b) 1.0% Ca (c) 1.5% Ca (d) 2.0% Ca

3.3. Microhardness study

Microhardness been performed using MATSUZUWA model MMT-X7 with diamond pyramid indenter and 0.5Kg load, 15s dwell time, and the study was done to analyze the hardness variation with change in aging temperature with different Ca percentage i.e. 0.5,1.0,1.5 and 2.0 wt.%. The results shows that, increase in aging temperatures increases the hardness, and also increase in Ca addition increases the hardness and then subsequent decrease in hardness, this phenomena is observed same in aging temperatures of 180°C,200°C and 220°C except 240°C. The specimen aged at 240°C shows peak hardness at 1wt% Ca and then gradually decreases upon subsequence increase of Ca to 1.5 and 2%. The direct proportionality for aging temperature/Ca addition to hardness is due to the increasing chances of fine precipitates Al_2Ca .

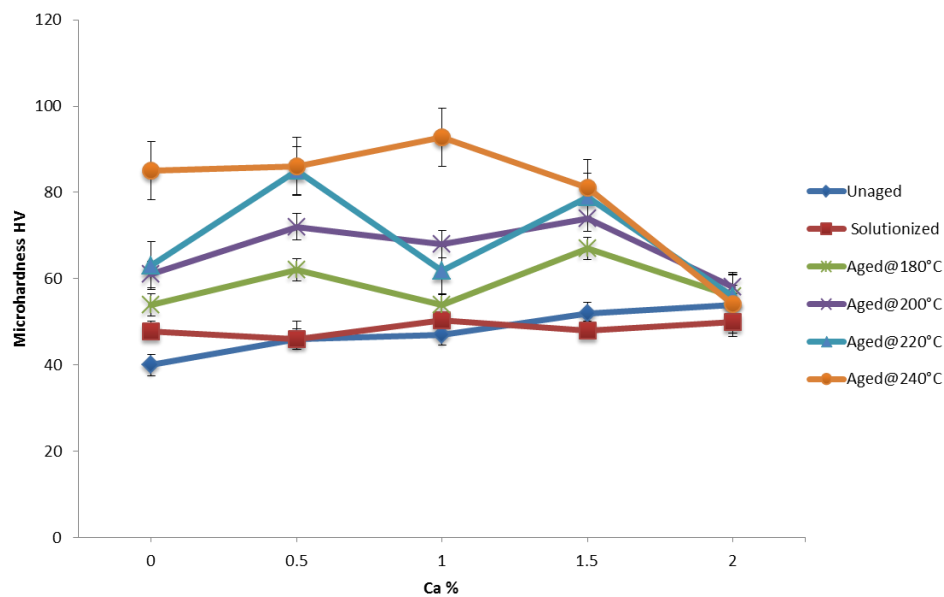


Fig.7. Microhardness Result:Effect of Ca Composition vs. Aging Temperature.

3.5. Immersion test results

The immersion test was carried out for the specimens in table 1 in 3.5 wt.% NaCl solutions, and the corrosion rate in terms of weight loss was presented in table 2. The results show that, AZ61+0.5%Ca aged at 200 °C shows the best corrosion resistance, than other stated conditions. The best result is due to presence of fine precipitates of sufficient Al_2Ca and discontinuity β . phase (corrosive) in Mg matrix.

Table 2. Corrosion Rate of Exposed samples

CORROSION RATE (mpy)					
Wt.% of Calcium	without aging	180° C	200° C	220° C	240° C
base	6048	5640	5423	7217	7021
0.5%	4079	3163	2659	6766	6521
1.0%	5804	4910	4767	5037	4886
1.5%	6607	6057	5417	5761	5883
2.0%	6933	6319	6191	6140	6377

3.6. SEM after immersion

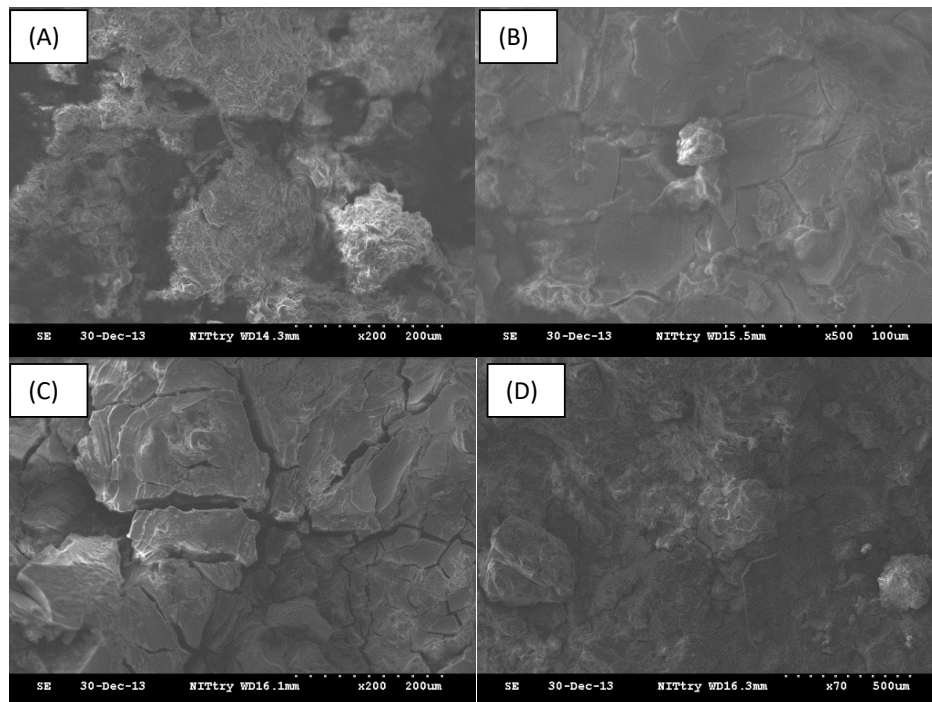


Fig.8.SEM images of AZ61+ XCa were aged at 180°C for 16 hrssamples after Immersion in 3.5 wt.% NaCl solution (a) 0.5 wt.% of Ca (b) 1.0 wt.% of Ca (c) 1.5wt.% of Ca (d) 2.0wt.% of Ca

CONCLUSION

1. Ca addition to AZ61 magnesium alloy refines the cell size and the $\text{Mg}_{17}\text{Al}_{12}$ phase. With Ca addition, a new Al_2Ca phase is formed and the amount of the $\text{Mg}_{17}\text{Al}_{12}$ phase decreases. The Al_2Ca phase

increases and is distributed along cell boundaries with increasing Ca content.

2. The β -Mg₁₇Al₁₂ phase was getting to distribute along the grain boundary discontinuously after treated at 420°C, ageing for 16 hour followed by air-cooling. After Solution treatment, β -Phase did not completely dissolve into α -Mg phase. The residual β -Mg₁₇Al₁₂ phase distributed along the grain boundary and had block like or island shapes. The size of α -Mg was getting to be coarser while increasing the aging temperature.
3. The refined microstructure results in the improvement of corrosion resistance on AZ61 magnesium alloy. Calcium added upto 1wt% of the AZ61 alloy improves the corrosion resistance of the alloy
4. Immersion test results shows that 0.5% Ca sample has better corrosion resistance than others.
5. Increased aging temperature coarsens the α -Mg as revealed on the microstructure. Finally samples aged at 200°C possess higher corrosion resistance compared to samples aged at other temperatures.

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