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# Degradation behavior of as cast and powder metallurgy processed Mg-Ca alloys

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**Abstract** – Biodegradability and mechanical properties similar to natural bone have made Mg alloys potential competitors for metal implant applications. Mg-Ca alloys are of interest as Ca is an essential element in the human body. However, an increased Mg<sub>2</sub>Ca secondary phase with increasing Ca addition results in pitting corrosion in these alloys. Reports suggest that Mg alloys with ≤ 1wt % Ca additions possess good degradation resistance. Hence, Mg-xCa alloys (x = 0.3, 0.6, 0.9 wt %) were fabricated by gravity die chill casting and powder metallurgy (PM) techniques. Their ‘mean degradation depth, *h* (μm)’ values were measured by immersion test. Physiological cell-culture medium DMEM+ Glutamax with proteins (10 % FBS) and an incubator were adopted for conducting the test. The volume fraction of Mg<sub>2</sub>Ca was calculated with Image J image analysis software. Results show that degradation behavior is influenced by the amount of secondary phase and its distribution in the Mg matrix. PM alloys showed homogenous degradation compared to the as cast alloys. The highest degradation resistance was exhibited by PM processed Mg-0.3Ca alloy with lowest *h* value of 0.39 μm. A long-term immersion test revealed the ‘mean degradation rate,  $\dot{h}_{\infty}$  (μm/day)’ as 0.51 μm/day.

**Keywords** – cell culture medium, in vitro, long term immersion test, mean degradation depth, powder metallurgy, sintering.

## 1. INTRODUCTION

Magnesium alloys show decent degradation resistance in dry atmosphere because of the formation of a stable and reasonably protective oxide layer on their surfaces. The main limitation of magnesium alloys for biomedical application is their poor degradation resistance under wet atmospheres or physiological conditions. Hydrogen evolution and formation of galvanic circuits between the secondary phases and the matrix make the degradation a more complex mechanism. The degradation kinetics depend on the microstructure of the alloy which in turn depend on the material processing parameters. Though a good amount of literature is available relating the degradation reactions to the microstructure of cast and heat treated Mg alloys [1, 2], little is known about the same with respect to PM processed Mg alloys. With sintering of Mg made feasible [3], various Mg alloys were fabricated by PM technique and investigated for their mechanical properties and degradation behavior. For the present study, Mg-Ca alloys were produced and their physiological degradation behavior is compared to their as cast counterparts. Please note that the alloy compositions indicated in this article are in weight percentages unless otherwise stated.

**Aim of the study:** To evaluate the degradation behavior in as-cast and PM processed Mg-xCa alloys (x = 0.3, 0.6, 0.9 wt %) through immersion test procedure and to correlate the observations to the alloys microstructural features.

The hypotheses of the study were:

- (1) With increasing Ca rich phase at the grain boundary, a fine-grained microstructure with increased grain boundary area per unit volume of the alloy decreases the degradation resistance of the alloy.
- (2) Uniform distribution of secondary phase particles hinder the continuous degradation of Mg matrix and eventually slows down the degradation process.

## 2. MATERIALS AND METHODS

### Materials

As cast Mg-Ca alloys were gravity die chill casted in neutral Ar+SF<sub>6</sub> atmosphere. The ingots were machined to 15mm\*10mm (length\* diameter) cylinders. For the fabrication of PM alloys, pure Mg powder and a pre-alloyed Mg-10Ca master alloy powder were mixed in proportion to their weights to obtain the desired final compositions in alloys. The starting materials are shown in Table I below.

TABLE I  
SHAPE AND SUPPLIER OF RAW MATERIALS

Powders	Particle shape and size	Manufacturer
Pure Mg	spherical powder <45 μm	SOCIÉTÉ POUR LA FABRICATION DU MAGNÉSIUM, MARTIGNY.
Master alloy powder	spherical powder 45-63 μm	ZENTRUM FÜR FUNKTIONSWERKSTOFFE GEMEINNÜTZIGE GMBH, CLAUSTHAL, GERMANY AND HZG.

## Methods

### Specimen preparation and sterilization

- The cylinders of as cast alloys were machined to 2 mm\*10 mm (length\*diameter) discs. These served as immersion test specimens.

- For PM fabrication, cylindrical green specimens were produced initially by pressing the powder mix at a uniaxial surface pressure of 175 MPa with an air hydraulic (Enerpac RC55, Milwaukee, USA). This was done under Ar 4.6 protective atmosphere to limit the contact with atmospheric oxygen. Sintering runs were carried out for 64 h under Ar 6.0 atmosphere at ambient pressure conditions (XRetort, Xerion, Germany). Sintering temperatures employed were 642 °C and 623 °C for Mg-0.3Ca, Mg-0.6Ca and Mg-0.9Ca alloys respectively as shown in Figure 1. After sintering, cylindrical discs of 2 mm\*10 mm (length\*diameter) were cut out for immersion test.

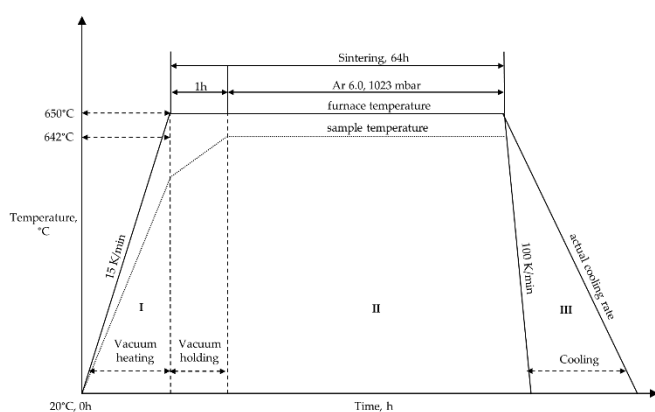


FIGURE 1

EXAMPLE SCHEMATIC OF THE SINTERING RUN FOR Mg-0.3Ca ALLOY INDICATING STAGE I—VACUUM HEATING, STAGE II—SINTERING UNDER AR 6.0 ATMOSPHERE AND STAGE III—COOLING [4]

- All immersion test specimens were ground using 2500 SiC paper to ensure the same surface condition prior to the test.

- Cleaning procedure was carried out using organic solvents of cyclohexane and acetone. Samples were ultra-sonicated in each reagent for 20 min. Sterilization of the samples was performed in 70 % ethanol as reagent.

### Immersion test

- Immersion test was adopted as the standard method for evaluating the degradation behavior of the fabricated Mg-Ca alloys. Dulbecco's Modified Eagle's Medium (+ 4.5 g/L D-Glucose, + Pyruvate) supplemented with 10 % FBS (Fetal Bovine Serum) was employed as physiological cell culture medium. Additionally, 1 % Penicillin Streptomycin was added to the medium to prevent bacterial contamination. The well plates with samples immersed in the medium are then transferred into an incubator containing cell culture conditions (37 °C, 20% O<sub>2</sub>, 5% CO<sub>2</sub>, 95% relative humidity) for 3 days.

Instead of calculating the corrosion rate (mm/year) as stated by ASTM NACE/ASTM G31-12a standard [5], the mean degradation depth,  $h$  (μm) was calculated using the formula below [4].

$$h = \Delta m / A \cdot \rho \quad (1)$$

Here,  $\Delta m$  is the mass loss of the sample before and after immersion test (g),  $\rho$  is the density of the alloy (g/cm<sup>3</sup>),  $A$  is the surface area of the sample exposed to the cell culture medium (cm<sup>2</sup>).

### Characterization techniques

- Surface morphology before immersion test was examined under optical microscopy. Grain size measurements were conducted by slope intercept method. Degradation morphologies after immersion test were visualized under BSE mode scanning electron microscopy (Phenom PROX, Eindhoven, The Netherlands).

## 3. RESULTS

From the optical micrographs, the measured grain sizes of as cast Mg-Ca alloys were 496 μm, 182 μm and 108 μm for Mg-0.3Ca, Mg-0.6Ca and Mg-0.9Ca alloys respectively. The uniform distribution of the secondary Mg<sub>2</sub>Ca precipitates can be visualized within the grains and at the grain boundaries in as cast alloys as shown in Figure 2.

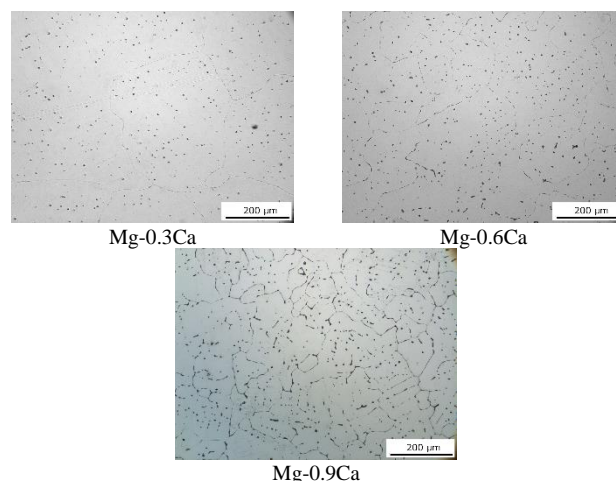


FIGURE 2

OPTICAL MICROSTRUCTURES OF AS CAST Mg-Ca ALLOYS. THE INCREASE IN SECONDARY PHASE WITH INCREASING Ca CONTENT CAN BE SEEN DISTINCTIVELY AS DARK AREAS IN Mg MATRIX.

The influence of grain size on degradation of Mg alloys is still under debate in scientific community. Literature supports the cases of grain size both decreasing and increasing the degradation resistance in Mg alloys [6-9]. In the present study, though there is a huge decrease in the grain size of cast alloys with increasing Ca additions, the  $h$  values remained around 0.6 μm indicating no significant effect of grain size on degradation in these alloys. On the other hand, the increase in Ca percentage is increasing the amount of secondary phase in the alloy as shown in Table II.

TABLE II  
CALCULATED VOLUME FRACTIONS OF MG-CA ALLOYS FABRICATED BY  
CASTING AND PM ROUTES.

Processing route	Alloy	Volume fraction of secondary phase, %
As cast	Mg-0.3Ca	0.7
	Mg-0.6Ca	1.4
	Mg-0.9Ca	3.3
Powder metallurgy	Mg-0.3Ca	3.1
	Mg-0.6Ca	3.9
	Mg-0.9Ca	4.9

This is expected to advance the degradation because of the difference in electrode potential values of Mg<sub>2</sub>Ca precipitates and the Mg matrix. This difference causes the anodic dissolution of the Mg matrix. Therefore, the higher the amount of secondary phase, the higher is the degradation. However, the same phenomenon is not observed in the present study.

Grain boundaries being the high energy areas are the active sites for corrosion initiation. The increase in secondary phase at grain boundaries will aid in lowering the degradation resistance of the alloy. Both aspects lead to an increased *h* value from Mg-0.3Ca to Mg-0.9Ca. However, the similar tendency is not visualized in Figure 3 for as cast alloys. The alloys showed similar *h* values about 0.64 μm- 0.74 μm. The possible explanation is that at low Ca percentages, the homogenous distribution of the secondary phase in Mg matrix retards the corrosion attack. From Figure 2, the distribution appears homogenous in the as cast alloys. This uniform distribution creates discontinuous networks of corrosion sites preventing the corrosion propagation. However, it is not yet known if the corrosion progresses with increased immersion times beyond 3 days.

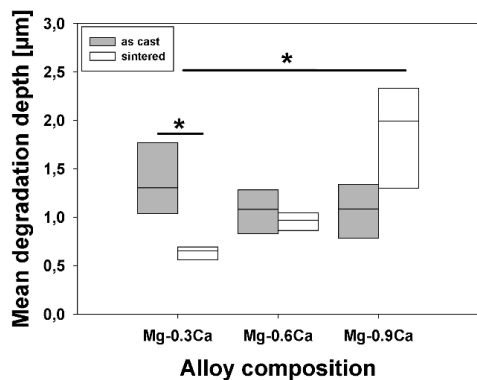


FIGURE 3

COMPARISON OF MEAN DEGRADATION DEPTH VALUES OF AS CAST AND PM PROCESSED MG-CA ALLOYS. NEARLY SAME VALUES ARE EXHIBITED BY CAST ALLOYS WHEREAS PM ALLOYS SHOWED AN INCREASING TENDENCY IN DEGRADATION WITH INCREASING CA CONTENT.

On the other hand, for PM processed alloys, the distribution of secondary phases is concentrated mainly at the grain boundaries as shown in Figure 4. The grain size remained the same in these alloys because of the same initial particle sizes of the powders used for production as shown in Table I. The measured grain sizes were 18.6 μm, 17.6 μm and 20.5 μm for Mg-0.3Ca, Mg-0.6Ca and Mg-0.9Ca alloys respectively with no statistically significant differences. Hence, the increase in degradation is attributed to the increase in secondary phases in these alloys. The *h* values calculated are 0.39 μm, 0.63 μm and 1.09 μm for Mg-0.3Ca, Mg-0.6Ca and Mg-0.9Ca alloys

respectively. The alloys exhibited low porosity values of <1 % with no significant difference. This is because different sintering temperatures were chosen for different alloys to promote the same amount of liquid phase during sintering.

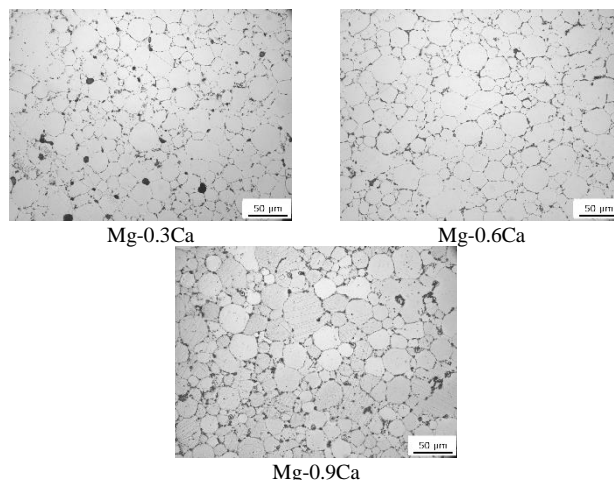


FIGURE 4

OPTICAL MICROSTRUCTURES OF PM MG-CA ALLOYS. FINE GRAINED MICROSTRUCTURE WITH POROSITY AND SECONDARY PHASE CONCENTRATION AT THE GRAIN BOUNDARIES BETWEEN THE PARTICLES.

Figure 5 shows the degradation morphologies after immersion test of as cast and PM processed alloys. Both alloys exhibited pitting type degradation behavior. However, the intensity of pitting and the size of the pit appears to be smaller in PM alloys compared to their as cast counterparts. This gives the first indication of a possible homogenous degradation in PM alloys.

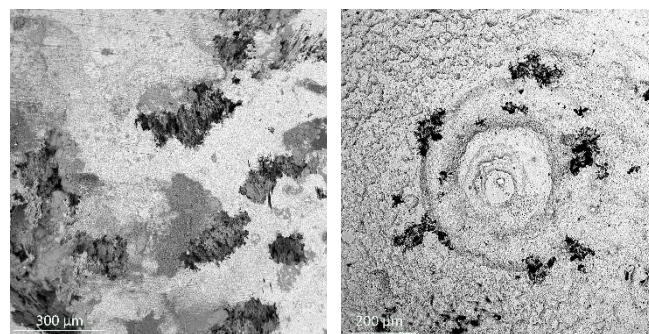


FIGURE 5

DEGRADATION MORPHOLOGIES AFTER IMMERSION TEST INDICATING PITTING CORROSION IN AS CAST ALLOYS (LEFT) AND PM ALLOYS (RIGHT). EXAMPLES ARE SHOWN FOR MG-0.3CA ALLOYS AFTER 3 DAYS IMMERSION TIME.

PM processed Mg-0.3Ca alloy showed lowest *h* value among all the six alloys investigated as shown in Figure 3. Hence, it was further scrutinized for its long-term degradation behavior for 42 days. The immersion test conditions maintained were the same as mentioned above in the Methods section, except for the exchange of old medium for the new medium every 3-4 days to represent semi-static test conditions by maintaining constancy in pH value of the medium.

From Figure 6, the phenomenon of linear degradation behavior is evident from the graph with blue line representing the linear regression fit for the blue data points measured using (1). The red dots are the calculated data by the analytical

expression, as in (2), to represent the similar degradation behavior [4].

$$h = h_0 \cdot \left(1 - e^{-\frac{h}{h_0}}\right) + \dot{h}_\infty \cdot t \quad (2)$$

Where,  $h$  = mean degradation depth,  $\mu\text{m}$   
 $h_0$  = degradation depth pertaining to initial reactions;  
 intercept value from the graph,  $\mu\text{m}$   
 $\dot{h}_\infty$  = mean degradation rate of the alloy; slope value  
 from the graph,  $\mu\text{m/d}$   
 $t$  = time of immersion,  $d$  (days).

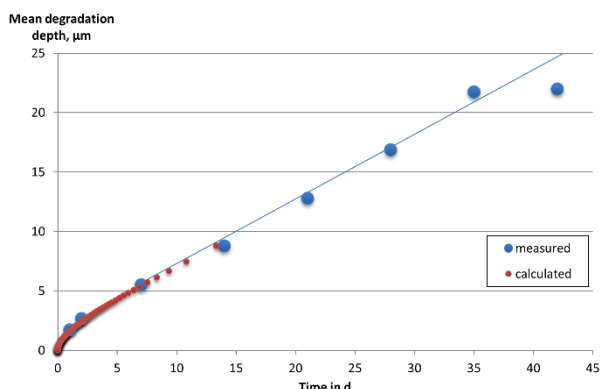


FIGURE 6

LONG TERM IMMERSION TEST RESULT FOR PM MG-0.3CA ALLOY AFTER 42 DAYS IMMERSION TIME SHOWING A LINEAR DEGRADATION BEHAVIOR AFTER 5 DAYS IMMERSION TIME. BLUE LINE REPRESENTS LINEAR REGRESSION FIT WHICH HAS A GOOD CORRELATION TO THE MEASURED DATA POINTS IN BLUE.

It is also evident that the alloy exhibits a near homogenous degradation from the fit of the linear regression to the measured data points. Another observation is that the degradation is much higher at short immersion times and attains a linear state after an immersion time about 5 days. This implies that the formation of degradation layer after initial reactions is aiding in lowering the degradation kinetics [10]. The mean degradation rate of the alloy was calculated to be  $0.51 \mu\text{m/d}$ .

#### 4. CONCLUSIONS

The results provide a preliminary insight into the mean degradation depths,  $h$  ( $\mu\text{m}$ ) and the degradation morphologies after basic immersion test experiments. This helps to qualify the alloys for cytotoxicity and cell compatibility tests in the future. The conclusions are as follows:

- The secondary  $\text{Mg}_2\text{Ca}$  phase plays an important role in controlling the degradation reaction kinetics in powder metallurgy processed alloys. Low Ca content is preferred for increased degradation resistance of the alloy.
- The as cast alloys are less prone to corrosion attack because of their near homogenous precipitate distribution during the final quenching stage of the casting process.
- The practice of a long-term immersion test made it feasible to calculate the mean degradation rate ( $\mu\text{m/d}$ ) of PM Mg-0.3Ca alloy which is a realistic value compared to the single time point measurement stated by ASTM NACE/ASTM G31-12a standard.
- It is beneficial to obtain a better understanding of the individual aspects of grain size and porosity dependencies on

the degradation of PM alloys which were not addressed in the present article.

#### Acknowledgment

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