Fabrication, microstructure and corrosion study of porous Mg-Ca-Zn using CaCO₃ pre-treatment with sodium trisilicate

A Erryani¹, I Al-aziz², F P Lestari¹, I Kartika¹

¹Research Center for Metallurgy and Material, Indonesian Institute of Science (LIPI) Kawasan Puspiptek Gedung 470 Serpong Tangerang Selatan, 15314, Indonesia
²Department of Metallurgy, Faculty of Engineering, University of Sultan Ageng Tirtayasa, Cilegon, Banten 42435.

E-mail: april011@lipi.go.id

Abstract. Magnesium-based alloys have the good potential as a biodegradable implant that can be degraded in biological tissue. In this research, the fabrication of porous implant materials based on Mg-Ca-Zn alloy develop by powder metallurgy. CaCO₃ as a foaming agent which previously coated by using sodium trisilicate has been used to obtain open cellular pores. The alloy compositions used in this research are Mg-Ca-3Zn-5CaCO₃ and Mg-Ca-3Zn-10CaCO₃. Sintering process is carried out at temperature of 600, 650 and 700 °C with holding time of 5h. The alloy is characterized by using XRD (microstructure analysis), SEM (surface and pore analysis) and corrosion test of alloys (electrochemical analysis using tafel graph). The microstructures of the alloy show MgO and Mg₂Ca phase SEM results show the pores in the alloy with the size approximately around 194.843-266.938μm. The corrosion rate in alloys is obtained in the range of 0.4-3.2 mmpy. The morphology of the alloy surface after corrosion process shows the volcano type. The corrosion process occurs localized where the electrochemical reaction occurs, so as to form a distinctive structure with the shape of the circle and the hole in the middle.

1. Introduction

Metal foams or porous metal are engineering material that have been unique combination of mechanical, physical and thermal properties [1]. These pure or alloy metals have shown a significant role in many parts of daily life, especially in the medical field such as material implant [2]. The chemical composition of implant determines the nature of the changes in the living body [3]. Metal alloys for the biomaterial should also have good corrosion resistance in an environment of tissues and body fluids and mechanical properties, which are required for load transfers [4][5].

One of the most widely used metal and alloy as an implant material is magnesium and magnesium alloys [6][7]. Magnesium has low corrosion resistant therefore its used in biomedical applications. Magnesium alloys have been regarded as materials for biodegradable orthopedic implants. High reactivity of magnesium in corrosive media can be used as an advantage [8]. Magnesium alloys have been regarded as materials for biodegradable orthopedic implants [8].

Biodegradable implant materials which were identical to porous materials have similar properties with human bones. It is expected that porous materials are also capable of fossilization in the process of growth of new bone tissue [9]. Cellular metals and metal foams are metals with pores that are intentionally connected in their structure. The terms cellular metals or porous metals are general
expressions referring to metals having large volume of porosities, while the terms foamed metal or metallic foams applies to porous metals produced with processes where foaming take place. Besides, the term metal sponge refers to highly porous materials with complex and interconnected porosity where the porosity cannot be subdivided into well-defined cells [10][11].

In this research, Mg Alloy foam was prepared by powder metallurgy method. Porous structure in Mg-Zn-Ca alloy can be obtained by using a foaming agent. Foaming process is performed with the gas-releasing agent and other additives that produce a foamed alloy, which differs greatly from the matrix alloy [12]. The foaming agent used in this study is CaCO₃ which was previously coated with a passive layer of SiO₂. SiO₂ passive layer was coated on the surface of CaCO₃ to decrease its foaming speed and conditioning the foaming process more simultaneously resulting in a more uniform pore size [13].

2. Material and Method
Mg, Zn and Ca as main alloys are mixed with CaCO₃ which serves as a foaming agent. The composition of alloys (wt.%) are Mg-Ca-3Zn-5CaCO₃, Mg-Ca-3Zn-10CaCO₃. Previously, CaCO₃ is coated using sodium trisilicate with sol-gel method. The alloying process is carried out by using powder metallurgy. Mixing process is done using a shaker mill for approximately 2 hours in order to obtain a homogeneous powder size in the alloy. Then, the alloys are compacted with a pressure of 100 MPa for 2 minutes and 200 MPa for 3 minutes. The green compact is heated in a tube furnace with the Argon atmosphere. Sintering process is carried out in the temperature of 600, 650 and 700 °C and holding time for 5 h. Rate of temperature rise in the furnace is 5º/ min. Phase analysis was performed using X-Ray diffraction technique (Shimadzu XRD-7000), while microstructure of alloys are characterized by using scanning electron microscopy (JEOL, JSM-6390A Japan).

Corrosion testing is performed using Gamry Instrument G750 according to ASTM G5-94 standard. Three electrode cells are used for corrosion measuring i.e; calomel electrode (SCE), graphite electrode (opposing electrode) and sample as with a pH of 7.4. The SBF solution temperature is 37 °C which is prepared using laboratory chemicals with the following composition:

| Component   | Composition (g/ml) |
|-------------|--------------------|
| CaCl₂       | 0.14               |
| KCl         | 0.4                |
| KH₂PO₄      | 0.06               |
| MgCl₂.6H₂O  | 0.1                |
| MgSO₄.7H₂O  | 0.1                |
| NaCl        | 8.0                |
| NaHCO₃      | 0.35               |
| Na₂HPO₄     | 0.048              |
| Glucose     | 1.0                |

Microstructures of the alloy after corrosion testing were observed by using scanning electron microscopy (JEOL, JSM-6390A Japan).

3. Results and Discussion

3.1 X-Ray Diffraction Analysis
XRD analysis is used to determine the phase or crystals formed after various temperatures sintering process of 600, 650 and 700°C with a 5-hour holding time in Mg-Zn-Ca alloys with CaCO₃ coated by natrium trisilicate (Figure 1-3).
In general as shown in Figure 1, Mg and MgO phases was obtained in the XRD pattern, while the Mg2Ca was revealed in the alloys at sintering temperature of 700°C. The predominantly formed Mg phase in the alloy is due to Mg element as base metal, whereas Zn and Ca are merely small metal compositions.

The lattice formed of Mg crystallographic system is Hexagonal, with an average distance between lattices of a = 3.2093 Å and MgO is cubic—with the distance between atoms a = 4.2112 Å. The MgO indicates that oxygen is still presented during sintering process. MgO in its manufacture is avoided because it can decrease the mechanical properties of Mg-based materials. The non-toxic MgO oxide in the body only affects the mechanical properties of the implant [14].

3.2 Scanning Electron Microscopy Analysis
Figure 3 shows SEM results of Mg-3Zn-1Ca-5CaCO3-coated with natrium trisilicate at various sintering temperatures with 5 h holding time.
Figure 3. SEM Micrograph of Mg-Ca-Zn-5CaCO$_3$ at 600°C (a, b), 650°C (c, d), 700°C (e, f).

The analysis performed by SEM shows that the alloy composition has a large pore cavity of 254μm at 600°C (figure 3a), slightly different from the pore size that is in figure 3 (c) with average size of pores approximately around 266 μm at 650°C. As shown in figure 3 (e), the alloy at temperature sintering of 700°C has pores with a fine structure and uniform compared to the structures in figure 3 (a) and 3 (c). These result approved that pretreatment in foaming agent can obtain homogeneous of fine pore structure. Meanwhile, the pore size obtained in the previous study showed that the average pore size without pre-treatment SiO$_2$-Coated CaCO$_3$ at 600°C and 650°C was 10-158 μm and 15-168 μm [15].

This difference in number and distribution is influenced by the difference in sintering temperature, along with the temperature sintering allowing the number and distribution of pores to be formed to be larger. Temperature of 700°C the pore number decreases this is due to the sintering critical temperature in the use of CaCO$_3$ foaming agent. Critical temperature is evaluated from the comparison of base metal melting temperature of Mg of 650°C and the sintering temperature variation of CaCO$_3$ which is used is 700°C with a holding time of 5 hours so that the formed pore is shrinkage because Mg having melting temperature below the decomposition temperature of CaCO$_3$. 
SEM analysis with 100x magnification seems to be seen that the pores are very diverse. The number and distribution of pores formed in this study have characteristics as shown in figure 4 (a) more evenly and larger than Figure 3.4 (c) while figure 3.4 (e) shows a larger pore size than the size and distribution of pores 3.4 (a). The average size of the pores formed by the addition of 10% wt of CaCO$_3$ coated natrium trisilicate at sintering temperature is 83.1147μm at 600°C, 103.08μm at 650°C and 195.335μm at 700°C. Table 3.1 shows the comparison of average pore size that can be with the composition of foaming agent 5 and 10%.

Figure 4. SEM Micrograph of Mg-Ca-Zn-10CaCO$_3$ at 600°C (a, b), 650°C (c, d), 700°C (e, f).
Table 2. Porosity of Mg-Ca-Zn-CaCO₃ alloys.

| Temperature (°C) | Mg-Ca-Zn-CaCO₃ |  |  |
|-----------------|----------------|---|---|
|                 | 5 wt. % (µm)  | Range (µm) | 10 wt. % (µm) | Range (µm) |
| 600             | 254.942        | 111.8 – 513.26 | 83.115        | 30.07 – 140.01 |
| 650             | 266.938        | 107.81 – 429.9 | 103.080       | 70 – 141.72    |
| 700             | 194.843        | 79.92 – 393.49 | 195.335       | 110.65 – 255.56 |

Table 2 show the pore size comparison between 5 wt. % and 10 wt. % of coated CaCO₃ in these alloys after sintering. Mg can still be stable with the growth of pores throughout the base metal, so that the pores formed do not experience of shrinkage. The influence of temperature may also lead to the possibility of smaller pore size. As shown on that table that in the temperature of 700°C at a composition of 5wt% coated CaCO₃ smaller pore size was formed. In the addition of foaming agent up to 10wt.% coated CaCO₃ at 700°C is related to the decomposition of CaCO₃, it takes time and sufficient heat energy to decompose CaCO₃ into gas and form pores.

3.3 Electrochemical Analysis
Electrochemical test is performed to determine the rate of corrosion of implanted material to the simulated body fluid. Mg is one of the most reactive metal elements, meaning that this metal is easily oxidized and very easily degraded in the body due to direct contact with human biological system.

![Figure 5. Corrosion rate of Mg-Ca-Zn-CaCO₃ alloys.](image)

Figure 5 shows an increase in corrosion rate at a temperature of 700°C. This is thought to be due to the high shaft count and MgO and Mg₂Ca phase formation more than the other two temperatures there by impacting low corrosion resistance compared to 600°C and 650°C temperatures. The lowest corrosion rate is found in the composition of 5% foaming agent with 650°C sintering temperature. The lower corrosion rate is due to the more uniform pore size and the influence of the less intermetallic phase generated (MgO and Mg₂Ca). Therefore, it can be said that the alloy composition with 5% foaming agent and sintering temperature of 650°C is the optimum corrosion rate generated.
3.4 Corrosion Morphology
After exposure in Hank's solution, the material surface looks rough and corrosion occurs. The pore structures that form on the surface of the alloy after corrosion like volcano. The results show that the corrosion is localized, as shown in figure 6 where Mg concurrent dissolution occurs with the evolution of H₂. The evolution of H₂ occurs when bubbles form. The bubbles of H₂ gas are formed on a specific surface or localized where electrochemical reactions occur, thus forming a distinctive structure with a circular shape and a hole in the middle [16].

![Figure 6. SEM micrograph of Mg-Ca-Zn-CaCO₃ alloys after exposure in Hank's solution.](image)

Evolution of H₂ is always from cathodic, then with a second phase with a spherical structure is the water reduction area acting as a cathode.

\[
\begin{align*}
\text{Anodic: } & \text{Mg} \rightarrow \text{Mg}^{2+} \text{ dan } 2e^- \\
\text{cathodic: } & 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \\
\text{Product: } & \text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2
\end{align*}
\]

According to the cathodic reaction in equation 2, generally local pH increases because of the OH⁻ ions. As a result, corrosion products are easily formed in the second phase area. The Mg(OH)₂ formation is stimulated by cathodic reduction of water liberating OH⁻ and by Mg²⁺ free anodic corrosion.

In addition to the Mg(OH)₂ formation, other corrosion products formed during the metals exposed in Hank's solution are O, Ca, P and Mg. The presence of OH⁻ on the Mg surface causes the transformation of HPO₄²⁻ into PO₄³⁻. It is desirable that Ca²⁺ and PO₄³⁻ ions diffuse from Hank's solution to the Mg surface and coalesce in the Mg(OH)₂ layer which is a corrosion product. The solubility of
Ca₅(PO₄)₃(OH) and Mg₅(PO₄)₂ products is less than Mg(OH)₂ [17]. Thermodynamically, Ca₅(PO₄)₃(OH) and Mg₅(PO₄)₂ are more stable than Mg(OH)₂. So it can be said that the final product of corrosion is Mg(OH)₂, Ca₅(PO₄)₃(OH) and Mg₅(PO₄)₂[18].

4. Conclusion

Mg-Ca-Zn alloy using CaCO₃ coated natrium trisilicate as foaming agent are successfully fabricated by using powder metallurgy method. The phase analysis results using XRD show MgO and Mg₂Ca phases on the alloy. SEM results show the formation of pores from the decomposition of CaCO₃ as a foaming agent with the size approximately around 194.843-266.938μm. The corrosion rates of this alloy obtained in the range of 0.4-3.2 mmpy. The morphology of the alloy surface after corrosion process shows a volcano type. The corrosion process occurs localized where an electrochemical reaction occurs, so as to form a distinctive structure with the shape of the circle and the hole in the middle.

References

[1] Yang D, Yang C and Hur B 2008 Mater. Sci. Techno. 24 302–304
[2] Orinak A, Orinakova R, Kralova Z O, Turonova A M, Kupkova M, Hrubovkakova M, Radonak J, and Dzuunda R 2014 J. Porous Mater 21 131–140
[3] Gonzalez S, Pellicer E, Suriach S, Bar M D and Sort J 2013 Bio. and Mech. Int. of Mag. and 12
[4] Nowosielski R, Cesarz R, Babillas K 2013 J. Achiev. Mater. Manuf. Eng. 58 7–15
[5] Zander D and Zumdick N A, 2015 Corros. Sci. 93 222–233
[6] Sahinoja M T 2013 Tampere University Of Technology
[7] Zivić F, Grujiović N, Manivasagam G, Richard C, Landoulsi J and Petrović V 2014 Tribol. Ind. 36 (1) 67–73
[8] Wang H and Shi Z M 2008 Mater. Forum 34 100–104
[9] Erryani A, Pramuji F, Amur D, Amal M I, and Kartika I 2017 IOP Conf. Ser. Mater. Sci. Eng. 202 012028
[10] Lefebvre J, Banhart L P and Dunand C David 2008 Adv. Eng. Mater. 10 775–787
[11] Zhao X, Shi L L and Xu J 2013 J. Mech. Behav. Biomed. Mater. 18 181–190
[12] Seyedraoufi Z S and Mirdamadi S 2013 J. Mech. Behav. Biomed. Mater. 21 1–8
[13] Lu G Q, Hao H, Wang F Y and Zhang X G 2013 Trans Nonferrous Met. Soc. China 23 1832–1837
[14] Niederlaender J, Walter M, Krajewski S, Schweizer E, Post M, Schille C, Geis-Gerstorfer J and Wendel H P 2014 J. Mater. Sci. Mater. Med. 25 835–843
[15] Erryani A Lestari F P, Anmur D and Kartika I, Sriyono 2015 Proceeding 2nd Int. Conf. Mater. Metall. Technol. 423–434
[16] Noviana D, Paramitha D, Ulum M F and Hermawan H 2016 J. Orthop. Transl. 5 9
[17] Fajardo S and Frankel G S 2015 Electrochim. Acta 166 403
[18] Hou L, Li Z, Pan Y, Du L, Li X, Zheng Y and Li L 2014 Prog. Nat. Sci. Mater. Int. 24 466–471

Acknowledgment

The author would like to thank for the financial support by Excellent Research Program of Indonesian Institutes of Sciences (UNGGULAN LIPI) 2017. This paper was supported by Research Center for Metallurgy and Materials – LIPI, especially biocompatible implant research group.