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Degradation and Corrosion of Biodegradable Metal Zn-xCa

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Abstract. Zn-based biodegradable metals (BMs) are considered as new potential in osteosynthetic implant devices. In this study Ca, which acts as an essential element in the human body, is used to improve the rate of Zn degradation and corrosion. The alloy was synthesized using the powder metallurgy method with two different processes: cold pressing followed by sintering (CP-S) and hot isostatic pressing (HIP). Microstructure properties, as well as in vitro degradation and corrosion were studied to determine the effect of adding Ca. Variations in the sample consist of Zn-0.5Ca, Zn-1Ca, Zn-1.5Ca and Zn-2Ca. The results and analysis of test data show that the addition of Ca increases the rate of corrosion and degradation of the materials. Better bonding and microstructure properties are obtained in Zn-2Ca samples which form CaZn13 phases and small porosity. As for the HIP process, a better microstructure is obtained compared to CP-S.

INTRODUCTION

Biodegradable metal has shown very rapid development in this decade and is a promising material for various uses as an implant material. Initially iron-based BM (Fe) and followed by BM on a magnesium (Mg) basis, which is then followed by zinc-based BM (Zn). One of the motivations for the use of Zn is because it has a standard electrode potential value between magnesium and iron: Mg (-2,37 V) < Zn (-0,763 V) < Fe (-0,440 V). which means that the rate of zinc degradation is faster than iron and slower than magnesium, so that it suits clinical needs. More than that Zn has been widely known as an element of nutritional biological functions of the human body, among others, associated with nucleic acid metabolism, bone metabolism and others. One improvement effort is to make Zn-based alloys so that they can meet the demands of bone implantation and other biomedical applications.

Li, H.F. et al. (2015) has conducted research on Zn-X binary alloys using a casting method with several alloying elements, including Mg, Sr and Ca, and the Zn-1X binary alloy. The corrosion potential for Zn-1Mg, Zn-1Ca, and Zn-1Sr are -999 mV, -1019 mV, -1031 mV respectively, is lower than that of Zn (-998 mV). Lower corrosion potential indicates a material is more susceptible to corrosion. The Zn-1Ca binary alloy has a corrosion potential between Zn-1Mg and Zn-1Sr alloys, so Zn-1Ca is quite well applied as a bone implant. In addition, the element of calcium which is an essential element in the body has a very important role in bones, which is to determine bone density and strength

This research was conducted to improve the microstructure properties of Zn-Ca alloy using the powder metallurgy method using the cold pressing - sintering (CP-S) method, and hot isostatic pressing (HIP), and uses variations in the composition of the Zn-xCa binary alloy. The characterizations used in this study include SEM-EDX and XRD tests, as well as in vitro degradation and corrosion

MATERIALS AND METHODS

Material and Processing

Zn-xCa alloy synthesis, using the powder metallurgy method with the synthesis material used is Zn powder (Merck 95%, particle size of 45 μm) and granular Ca (Sigma Aldrich 99%). The first stage of processing the material is pre-treatment of calcium synthesis from granular to powder using a mechanical method (milling) for 2 hours by vacuum process and the flow of argon UHP gas in the vial to produce calcium powder with a size of about 74 μm. In the synthesis phase of Zn-xCa alloy, pure calcium powder (which has been synthesized using the best process of the three processes carried out) is mixed with pure zinc powder use High Energy Milling (HEM) for 3 hours with the aim of homogenizing the alloy. Alloy samples are Zn-0.5Ca, Zn-1Ca Zn-1.5Ca, and Zn-2Ca. The compacting process was carried out with two different processes, namely cold pressing - sintering (CP-S) and hot isostatic pressing (HIP). In CP-S, compacting with a pressure of 100 MPa with detention for 10 minutes. Next, the sintering process is carried out for 1 hour at a temperature of 320℃ using a furnace (flowing with argon gas) with the sintering rate of 5℃/min. As in the CP-S process, alloy

samples using the HIP process are compacted at a pressure of 100 MPa and a temperature of 320°C for 1 hour. Compaction in the HIP process using a compacting device equipped with a thermocouple (without argon gas flowing) with a maximum temperature of 320°C.

Microstructural characterization

XRD testing was carried out on Zn-xCa alloys to determine the phase and size of the crystals formed in the alloy after the CP-S and HIP processes. The XRD test results analyzed using two different methods, namely search-match using application program and manually.

Corrosion Testing

Corrosion testing aims to determine the level of corrosion that occurs in Zn-xCa alloys. This test is very important for almost all metals. This is because each metal element has its own level of corrosion which depends on the level of corrosion resistance of a metal. Corrosion testing was performed using a potentiostat electrochemical method at 37oC in an SBF solution with a sample area of 1.54 cm2 and the sample density depends on the sample composition. Potentiodynamic polarization tests were carried out at a scanning rate of 1 mV/s using a SBF solution. Preparation of SBF solution using hot plates and magnetic stirrers with a set temperature of 35°C.

In Vitro Degradation

In vitro biodegradation testing is one of the tests that is often done in bone implant applications. This test aims to determine the level of degradation or mass loss in the sample. In vitro degradation testing was carried out for 4 consecutive weeks. Measurement of the mass lost is done once a week. This is done because the material will bind bones and form apatite on its surface within 4 weeks.

RESULTS AND DISCUSSIONS

Microstructure

Based on the resulting XRD pattern, the phase formed for the Zn-xCa alloy with calcium composition from 0.5 wt% to 2.0 wt% is the $CaZn_{13}$ phase. Zn-0.5Ca alloys up to Zn-1.5Ca alloys are formed $CaZn_{13}$ phase only at one peak, either the CP-S method or the HIP method, which is at an angle of 54°. Whereas the Zn-2Ca alloy has 2 peaks of $CaZn_{13}$ phase on HIP and 5 peaks $CaZn_{13}$ phase on CP-S (Figure 1). The $CaZn_{13}$ phase formed in the diffraction pattern of the alloy corresponding to the Zn-xCa alloy phase diagram for the given temperature and composition variations. Based on the Ca-Zn phase diagram, only the $CaZn_{13}$ phase will be formed with a Zn composition between (92-100) wt% with a maximum temperature of 419.58°C. The formation of new phases indicates changes in the properties of the material, both physical, chemical and mechanical.

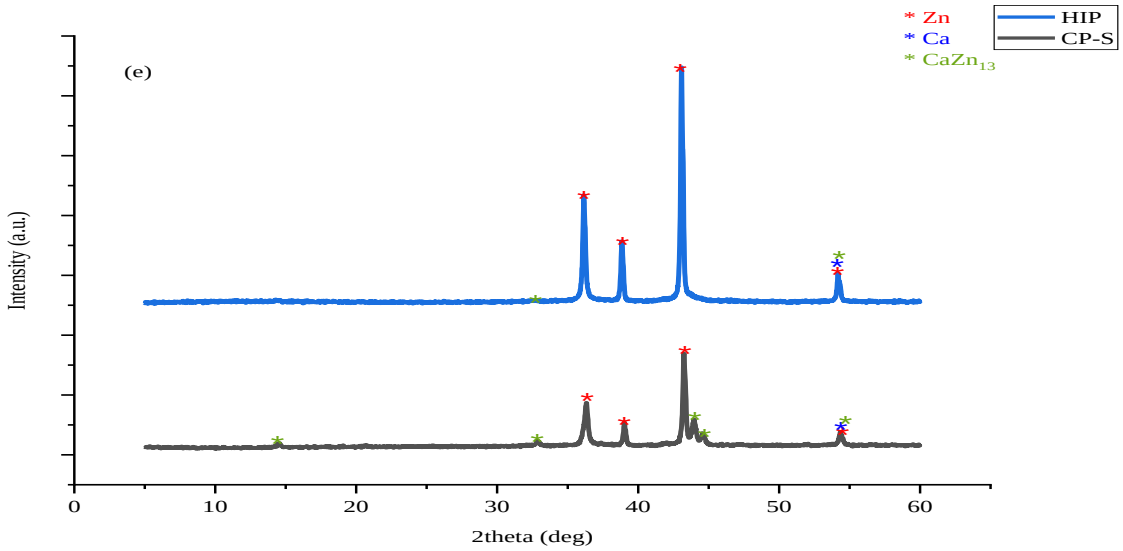

FIGURE 1. XRD of Zn-2Ca Pattern

Degradation

EDX testing on Zn-2Ca samples detected homogeneous elements of zinc and calcium. Element quantities obtained through EDX testing are listed in Table 1 and Table 2. Based on the atomic concentration data from the EDX test before degradation, CaZn6 for Zn-2Ca was obtained using CP-S and $CaZn_{13}$ for Zn-2Ca using HIP. The phases formed in Zn-2Ca through HIP correspond to the Ca-Zn binary phase diagram data, however for Zn-2Ca alloys via CP-S a compound which is not compatible with the Ca-Zn phase diagram is obtained. Therefore, the concentration of Ca atoms in Zn-2Ca alloys obtained using the CP-S method is likely due to the deposition of these elements in this area. The difference in the surface of the two materials with the same composition is very prominent due to the porosity formed in the two materials. Material treated with CP-S has a fairly small porosity, whereas those prepared by the HIP process tend to have a much greater porosity.

SEM-EDX testing after degradation was carried out to determine the morphology of the samples after degradation testing SEM test results after degradation, as in Figure 2, show the existence of apatite accumulation caused by in vitro degradation testing. Apatite formed indicates BM which has bioactive properties, namely material that has biological activities in the body. This is as stated by Zheng et al (2014) that the difference between permanent metal materials and BM is on interactions around the tissue, permanent metal material has bio-inert properties while BM has bioactive properties.

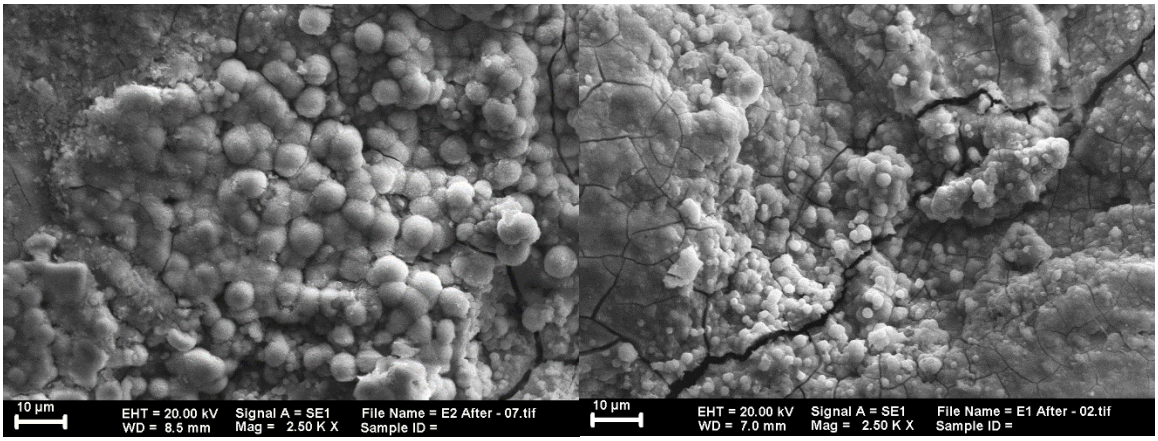

FIGURE 2. SEM Results of Zn-2Ca After Degradation (a) CP-S (b) HIP

From the test results it can be seen that in the tested area, it can be identified the number of elements formed as a result of degradation testing. These elements can be seen in Table 3 and 4. These elements are formed by ions in body fluids that interact with the material. Based on the data in the two tables it can be seen that the elements zinc (Zn) and calcium (Ca) have chemical compositions much lower than the elements oxygen (O). This is caused by the oxidation process during synthesis. In addition, the effect of the reagent on the solution also affects the amount of the composition of the oxygen element in the sample after degradation testing.

Basically, from the data concentrations formed atoms can be identified compounds formed. Some possible compounds formed are $ZnCO_3$, $CaCO_3$, $Zn(OH)_2$, $Ca(OH)_2$, ZnC_{l2}, CaC_{l2}, ZnO, CaO, $CaZn_{13}$, $Zn_3(PO_4)_2$, $Ca_3(PO_4)_2$, and many more.

TABLE 1. Test Results of EDX Zn-2Ca alloys using the CP-S Process

Element	Atomic Number	Unnormalized Concentration (wt%)	Normalized Concentration (wt%)	Atomic Concentration (at%)	Error (%)
Zn	30	85,15	90,65	85,59	2,9
Ca	20	8,79	9,35	14,41	0,3

TABLE 2. Test Results of EDX Zn-2Ca alloys using the HIP Process

Element	Atomic Number	Unnormalized Concentration (wt%)	Normalized Concentration (wt%)	Atomic Concentration (at%)	Error (%)
Zn	30	76,76	95,55	92,94	2,7
Ca	20	3,57	4,45	7,06	0,2

TABLE 3. EDX Test Results for Zn-2Ca (CP-S) alloys After Degradation

Element	Atomic Number	Unnormalized Concentration (wt%)	Normalized Concentration (wt%)	Atomic Concentration (at%)	Error (%)
Zn	30	34,07	35,47	14,96	1,0
O	8	29,06	30,26	52,16	3,9
Ca	20	15,00	15,62	10,75	0,5
P	15	9,24	9,62	8,57	0,4
Na	11	4,16	4,33	5,19	1,2
C	6	2,77	2,89	6,63	0,9
Mg	12	0,70	0,73	0,83	0,1
Cl	17	0,69	0,72	0,56	0,1
Al	13	0,20	0,20	0,21	0,0
Si	14	0,11	0,12	0,12	0,0
S	16	0,02	0,02	0,02	0,0
K	19	0,02	0,02	0,01	0,0

TABLE 4. EDX Test Results for Zn-2Ca alloy (HIP) After Degradation

Element	Atomic Number	Unnormalized Concentration (wt%)	Normalized Concentration (wt%)	Atomic Concentration (at%)	Error (%)
Zn	30	47,10	47,86	20,83	1,3
O	8	28,34	28,80	51,24	3,6
P	15	7,46	7,58	6,97	0,3
Na	11	7,42	7,54	9,33	1,7
Ca	20	3,54	3,59	2,55	0,1
C	6	3,24	3,29	7,79	0,9
Si	14	0,71	0,72	0,73	0,1
Mg	12	0,21	0,21	0,25	0,0
K	19	0,20	0,20	0,15	0,0
Cl	17	0,17	0,17	0,14	0,0
S	16	0,02	0,03	0,02	0,0
Al	13	0,00	0,00	0,00	0,0

In Vitro Degradation Test

This test is done immersing the sample for 4 consecutive weeks at 37°C in a SBF solution. To find out the reduction in sample weight, soaked samples are weighed once a week. The degradation test results can be seen in Figure 3.

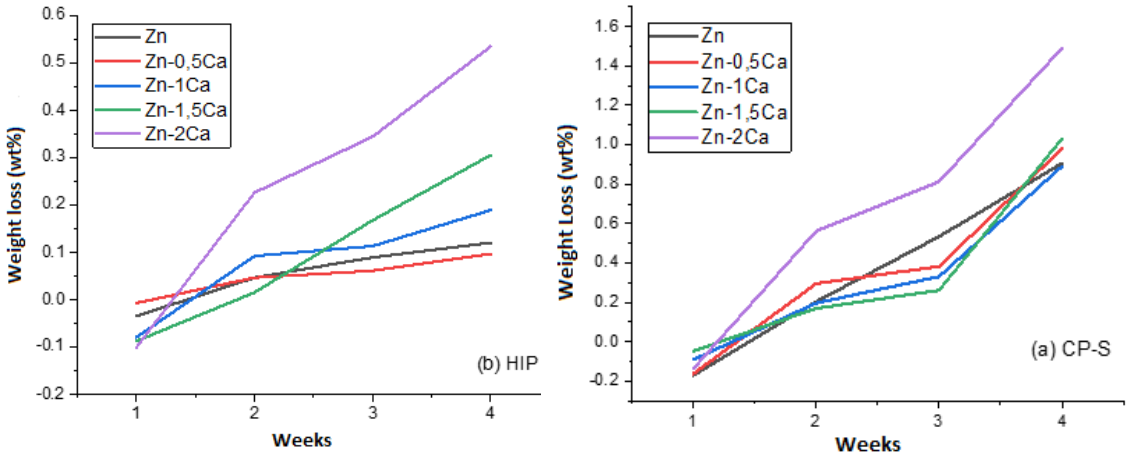

FIGURE 3. Reduction of In Vitro Degradation Test (a) CP-S (b) HIP

Weight reduction of Zn-xCa alloys continues to increase, both alloys with CP-S and HIP processes as seen in Figure 3. The weight reduction of the alloy indicates that the Zn-xCa alloy metal is a bioactive metal that is capable of being used for BM-based bone implant applications (Zheng et al, 2014). An increase in mass in all samples in the first week,

between 0.0072 g to 0.1705 g, then the mass decreases the following week. The increase in mass in the first week is predicted to be caused by the initial stages of formation of apatite on metal surfaces. At this stage, interactions between the solution / liquid in the body and the metal surface begin to occur, which causes the weight of the metal to increase. However, as time goes on metal absorption occurs due to organic molecules in the SBF solution. This process occurs on almost all metal surfaces which causes the metal to break bonds and there is a significant weight loss. These organic molecules, such as Cl^-, SO_4^{2-}, HCO_3^- or CO_2, will continue to absorb metal atoms so that the metal is fully degraded. Using this equation (1)

$$C = \frac{W}{\rho A t} \quad (1)$$

where C is the degradation rate mm/year, W is the weight lost, ρ is the density of the material, A is the area of the material, and t is the implantation/testing time, the degradation rate is obtained as shown in Figure 4.

In the CP-S process, Zn-xCa alloys have a greater degradation rate than Zn-xCa alloys that use the HIP process. Nevertheless, the rate of degradation of the alloy through CP-S is in a good range (Narayan, 1983), which is 0.15-0.5 mm/year. In addition, the rate of degradation increases with the addition of the calcium. The increased rate of degradation in the greater calcium composition is due to the standard potential of the Ca electrode which is much smaller than the potential of the Zn electrode. A small value on the standard potential of the Ca electrode indicates that the metal is more easily degraded. This causes the degradation rate of Zn-xCa alloys greater than Zn.

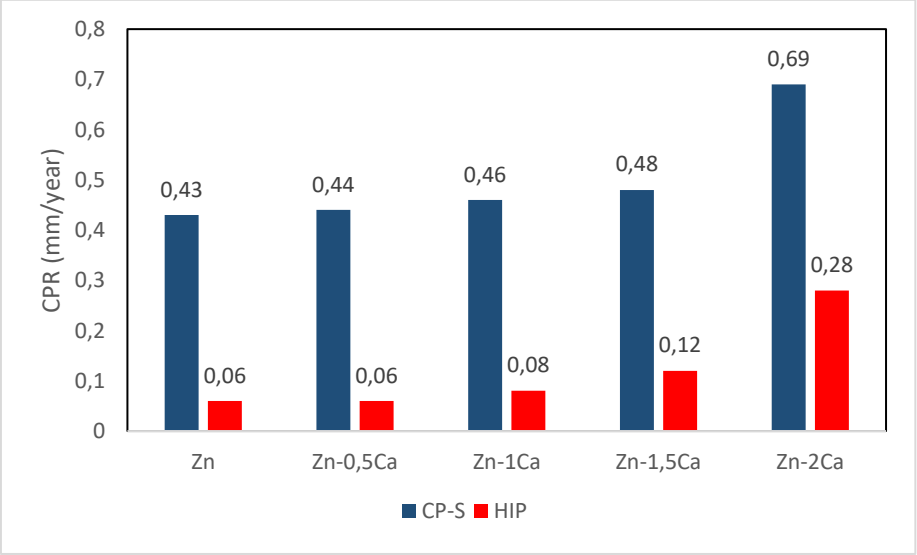

FIGURE 4. Degradation Rate of Zn-xCa Alloy

In Vitro Corrosion Test

In vitro corrosion testing aims to determine the corrosion rate of Zn-xCa alloys due to SBF solution. Corrosion test using Corrtest CS2530 Bipotatostat and the sample area used is 1.54 cm2, with material density not the same for each sample. The test results are in the form of a potential graph as a vertical axis and a current log as a horizontal axis, as shown in Figure 5.

From this graph, obtained E_{corr} corrosion potential, and corrosion current density, I_{corr} for each sample, so that the corrosion rate of each sample can be determined (Table 5) using

$$CPR = \frac{Mi_{corr}}{mF\rho} \quad (2)$$

where CPR is the metal corrosion rate (cm/s), M is the Molar mass of the metal, icorr is the corrosion current density (A/cm^2), m is the number of electrons involved in the corrosion reaction, F is the Faraday constant 96,490 C/mol, and ρ is the metal density (g/cm^3). Equation (2) can be changed so that the corrosion rate can be expressed in units of CPR (mm/year) with i_{corr} (mA/cm^2) is

$$CPR = 3,27\frac{Mi_{corr}}{mF\rho} \quad (3)$$

The corrosion rate / CPR (corrosion penetration rate) graph can be seen in Figure 6.

Based on data and calculations, the corrosion rate of Zn-xCa alloys is proportional to the addition of calcium (Ca), both CP-S and HIP, except Zn-0.5Ca and Zn-1Ca CP-S which have corrosion rates below Zn CP-S and Zn-0.5Ca HIP with corrosion rates below Zn HIP. The effect of adding Ca shows an increase in the rate of corrosion exactly on Zn-xCa alloys with x greater or equal to one. Thus, the low corrosion rate of zinc can be increased by the addition of calcium

in certain alloy compositions, so that the corrosion rate remains at the tolerance range used as bone imprint applications, i.e 3-24 weeks (Zheng et al, 2014)

Besides the influence of the composition of the alloy, the processing temperature at Zn-xCa also plays a role in the corrosion rate of the material. Alloys that formed by the CP-S process have a higher corrosion rate than materials formed by the HIP process only for Zn and Zn-2Ca. In contrast, Zn-0.5Ca, Zn-1Ca and Zn-1.5Ca alloys with the CP-S process have lower corrosion rates compared to the HIP process.

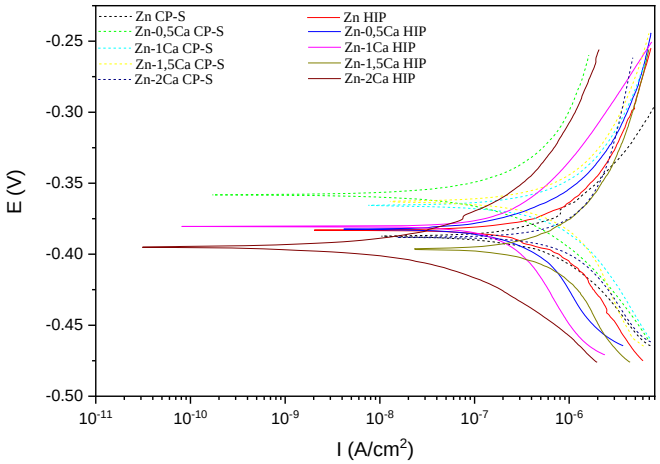

FIGURE 5. Results of Corrosion Rate Testing using Electrochemistry

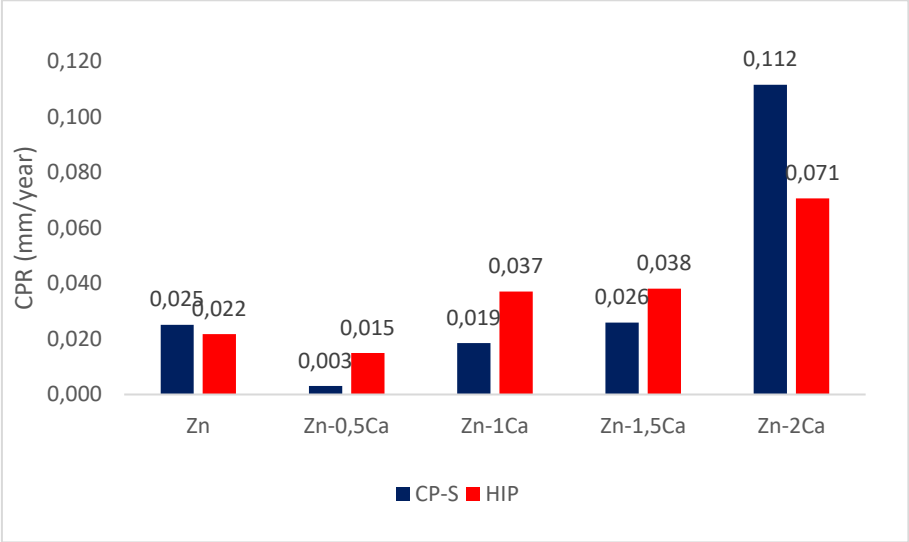

FIGURE 6. Zn-xCa Alloy Corrosion Rate

TABLE 5. Zn-xCa Alloy Corrosion Rate

	Sample	E_{corr} (V)	i_{corr} (mA/cm^2)	CPR (mm/year)
CP-S	Zn	-0,31948	1,68E-03	0,025
	Zn-0,5Ca	-0,10565	0,26E-03	0,004
	Zn-1Ca	-0,18765	1,20E-03	0,018
	Zn-1,5Ca	-0,19607	1,66E-03	0,026
	Zn-2Ca	-1,1365	7,03E-03	0,111
HIP	Zn	-0,14206	1,45E-03	0,021
	Zn-0,5Ca	-0,18557	0,98E-03	0,015
	Zn-1Ca	-1,0651	2,40E-03	0,037
	Zn-1,5Ca	-0,19922	2,44E-03	0,038

CONCLUSION

Zn-xCa alloy composition using powder metallurgy method has an influence on the microstructure, properties, and the rate of degradation and corrosion of alloys, both through CP-S and HIP. The rate of degradation and corrosion of the alloy increases with the addition of calcium to the percentage of weight between the two elements. Better bonding properties are obtained in Zn-2Ca alloys by the formation of $CaZn_{13}$. Corrosion rate with HIP process is higher than CP-S, while the degradation rate of alloys with HIP process is lower than CP-S. The better bonding properties of the Zn-xCa alloy are found in the Zn-2Ca alloy obtained by the CP-S process.

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