5-2022

Corrosion assessment of biodegradable metal implants for orthopedic applications

Wendy B. Reynoso-Diaz
University of Tennessee at Chattanooga, mkw818@mocs.utc.edu

Corrosion Assessment of Biodegradable Metal Implants for Orthopedic Applications

Wendy B. Reynoso-Diaz

Departmental Honors Thesis

The University of Tennessee at Chattanooga

Mechanical Engineering

Examination Date: April 08, 2021

Dr. Hamdy Ibrahim

Assistant Professor of Mechanical Engineering

Thesis Director

Dr. Mohammad Mahtabi

Assistant Professor of Mechanical Engineering

Committee Department Examiner

Table of Contents

1. Nomenclature

SBF - Simulated Body Fluid
PDP - Potentiodynamic Polarization
EIS - Electrochemical Impedance Spectroscopy
DI - Deionized
LP - Low Purity
HP - High Purity

2. Abstract

Magnesium alloys are the most promising materials to be used as biodegradable implants mainly due to their superior biocompatibility and lower specific density compared to other biodegradable metals (i.e., zinc and iron-based alloys). This study is investigating the effect of two different manufacturing methods and purity levels on the corrosion rates of a novel Mg-Zn-Ca-Mn-based alloy. Experimental *in vitro* corrosion tests were conducted on the biocompatible Mg-Zn-Ca-Mn-based alloy fabricated using conventional casting and hot rolling with low and high purity levels. The experimental research conducted, assessed the corrosion rates of the following Mg-1.2Zn-0.5Ca-0.5Mn-based alloys: Hot Rolled High Purity, As-Cast High Purity, As-Cast Low Purity, and Commercial Pure Magnesium. This was done using two testing methods, in vitro corrosion immersion testing and in vitro electrochemical testing. By doing so, the experiments aid in assessing how different purity levels or different manufacturing methods affect corrosion behavior. It was hypothesized that when comparing two magnesium-based alloys fabricated using different levels of purity, the high purity alloy would demonstrate a slower corrosion rate. Based on electrochemical testing and immersion testing, the hypothesis was proven to be true. It was also hypothesized that an alloy fabricated with a thermomechanical process would show slower corrosion rates than the as-cast ones. Based on electrochemical testing, this was proven to be false. Based on immersion testing, this was proven to be true, which provides more reliable data for corrosion rates. Data gathered aided in assessing corrosion rates of differently fabricated magnesium-based alloys. Further experiments should be conducted to determine the most desirable magnesium-based alloy fabrication.

3. Introduction

3.1 Background

Currently-in-use orthopedic implants are made of stiff and nonbiodegradable metals such as titanium and stainless steel. While these implants have been used for many years, their permanent existence in the body results in several complications after bone healing such as bone resorption, future implant fracture, and possible infection and inflammation [1]. Hence, the imperative need to develop temporary biodegradable implants that can eliminate such problems and enhance patients' treatment outcomes. Biodegradable metals are most suitable for use over temporary periods of time due to their superior mechanical strength and biocompatibility. This includes uses such as, vascular stents, bone fixtures, and bone grafting because in cases like these, human tissues/organs can regenerate themselves [2]. In addition, the implants used today (metallic or polymeric based) hinder the regrowth of bone and muscle around the implant. Meanwhile, biodegradable metallic metals are known to promote bone ingrowth. Biodegradable metals can be divided into 3 main families: magnesium, iron, and zinc-based alloys [2]. Magnesium alloys are the most promising materials to be used as biodegradable implants mainly due to their superior biocompatibility and lower specific density compared to zinc and iron-based alloys [3]. Some of the main problems that hinder the rapid development of magnesium-based bone implants are their relatively insufficient strength and fast corrosion rates in the physiological environment [4].

3.2 Research Question and Hypotheses

The research question for this experimental research is as follows: will the corrosion behavior of a patent-pending Mg-Zn-Ca-Mn-based alloy be the most suitable implant for biomedical use? It was hypothesized that a magnesium-based implant fabricated using a high purity alloy will have a

slower corrosion rate compared to a low purity one. It was also hypothesized that thermomechanical and heat treatment processes, known to increase strength, will enhance the corrosion behavior (slower corrosion rates) of magnesium-based alloys. Thus, the testing hypotheses become the following: **1)** the corrosion behavior of Mg-1.2Zn-0.5Ca-0.5Mn (wt.%) alloy samples fabricated with two different impurity levels were assessed using immersion and electrochemical tests and compared against that of commercially pure magnesium (control group), **2)** the corrosion behavior of Mg-1.2Zn-0.5Ca-0.5Mn (wt.%) alloy samples fabricated with two different manufacturing processes were assessed using immersion and electrochemical tests and compared against that of commercially pure magnesium (control group). To this end, the project aids to assess the corrosion behavior of a patent-pending biocompatible Mg-Zn-Ca-based alloys [5, 6] fabricated using different manufacturing methods.

4. Methodology

4.1 Testing

Methods used to conduct the research are as follows: in vitro corrosion immersion testing and in vitro electrochemical testing. The experimental research will be conducted using vitro immersion and electrochemical testing which falls into two categories: potentiodynamic polarization and electrochemical impedance spectroscopy. Potentiodynamic polarization (PDP) uses DC currents and is a voltage control technique where the electrode is polarized at a fixed rate over a range of potentials [7]. The current that flows through the cell in response to the electric field is recorded. Electrochemical impedance spectroscopy (EIS) is an electrochemical technique that measures the resistance of the component to AC currents. It evaluates the polarization resistance which is used

to determine the corrosion current density and corrosion rates [8]. Both methods are used due to learnings from past experiments.

4.2 Experimental Work Details (Immersion)

Experiments were conducted on the following Mg-1.2Zn-0.5Ca-0.5Mn-based alloys: Hot Rolled High Purity, As-Cast High Purity, As-Cast Low Purity, and Commercial Pure Magnesium. Immersion test coupons were cut from different shapes two being rods, one being a bar, and another being a sheet. The coupons were cut into different shapes but with similar surface area to decrease error when comparing results. Table 1 below provides average coupon dimension details for the alloys used in immersion testing.

Table 1: Coupon dimension details for immersion testing

TYPE	**SHAPE**	**Number of Coupons used**	**DIMENSIONS**				**Average Surface Area (cm^2)**
			Avg Length (cm)	Avg Width (cm)	Avg Diameter (cm)	Avg Thickness (cm)	
Hot Rolled High Purity	Rectangular	6	0.93	0.932	-	0.225	2.565
As-Cast High Purity	Rectangular	6	1.34	0.602	-	0.287	2.728
As-Cast Low Purity	Cylindrical	6	-	-	1.115	0.1995	2.656
Commercial Pure Mg	Cylindrical	6	-	-	1.126	0.196	2.689

As previously stated, in vitro immersion testing was conducted to determine corrosion rate in a simulated body environment. To do so, simulated body fluid (SBF) according to the following procedure:

Table 2: List of substances and their measurements needed to make a total of 2L of simulated body fluid (SBF)

Order	Name	Formula	Amount
1	Sodium Chloride	NaCl	10.806 g
2	Sodium Bicarbonate	NaHCO3	1.008 g
3	Sodium Carbonate	Na2CO3	0.852 g
4	Potassium Chloride	KCl	0.450 g
5	Potassium Phosphate Dibasic	K2HPO4	0.460 g
6	Magnesium Chloride Hexahydrate	Cl2H12MgO6	0.622 g
7	HEPES*	C8H18N2O4S	35.784 g
8	Calcium Chloride	CaCl2	0.586 g
9	Sodium Sulfate	Na2SO4	0.144 g
10	Sodium Hydroxide	NaOH	30 mL

*Combine 40 mL of Sodium Hydroxide and 160 mL of DI water into the 500 mL beaker then dissolve HEPES into this mixture before combining it into the bigger beaker (2000 mL)

The following materials were gathered before SBF preparation:

- 2000 mL beaker
- 500 mL beaker
- 1000 mL volumetric flask
- 150 mL graduated cylinder
- spoon

- Hot plate with magnetic stirrer
- PH meter
- Sensitive scale
- DI water
- Distilled water
- HCl
- Weighing cups
- Paper towels
- HCl solution

Before preparing the SBF, all three beakers were washed thoroughly with soap and water, and then rinse with deionized (DI) water. The 2000 mL beaker was filled with 1000 mL of DI water and then placed on hot plate. A stirrer was placed in the beaker and turned on. The hot plate was set to 100ºC and was set to spin at 300 rpm. After the water had reached the desired temperature of 100 ºC, all substances were dissolved one by one in the order given in Table 2 above. Each substance was completely dissolved before adding the next substance. All dry substance were weighted using weighing cups on a sensitive scale. To measure dry substances accurately, the clean weighing cup was measured first and then the substance was added. After each substance the weighing cup was re-weighed to ensure there isn't any substance left behind on it. After all substances were added and completely dissolved, the hot plate was turned off. Using the pH meter, the pH level of the solution was measured at 98ºF (37ºC) and adjusted till the pH level reached 7.4 at 98ºF. If the pH level needed to be lowered, HCl solution was added in small increments until desired pH level was reached. Then half of the solution (the first beaker should be roughly 600 mL) is transferred into the volumetric flask. DI water is added

until the solution reaches the 1000 mL marker on the volumetric flask. This is repeated with remaining solution, thus making 2L of SBF. Any unused SBF is refrigerated and stored in smaller closed containers.

Immersion testing was conducted for a total of 28 days, with data being gathered before experiment, at day 14, and at day 28. Before immersion, all coupons were polished sequentially using 400 to 2000 grit sized sandpaper. The coupons were then cleaned using alcohol and left to air dry. Initial measurements were taken right after, this includes weights and dimensions. The temperature of the test was held constant like that of body temperature (37ºC) by placing the testing beaker containing the coupons in a thermal incubator (Fisherbrand Isotemp Microbiological Incubator). The pH level was controlled at a level of 7.4 using an automatic pH controller (bluelab) that dispensed HCl when needed. Figure [1] below, shows the set up inside the incubator during immersion testing. The pH controller rested on the top level and the beakers remained in the middle level. Figure [2] shows the layout used to space coupons in the beaker to keep track of each coupon. The beaker was properly labeled, and each coupon was precisely placed to keep track of the coupons being tested.

Figure [1]: Sample of set up for immersion testing in the incubator.

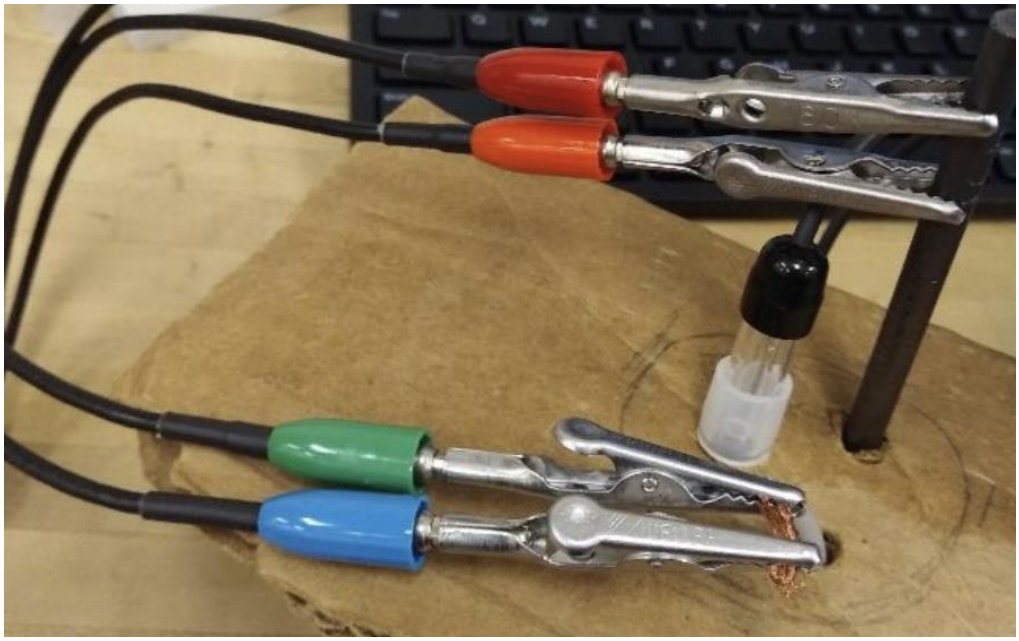
Figure [2]: Sample layout of coupons in immersion testing beaker.

The SBF was replenished every 3 days. The volume of SBF was determined by providing enough solution to have 50 ml of SBF per cm^2 of exposed surface area. This was done to exclude solution volume effect on corrosion behavior [9]. A total of 3 coupons from each type was collected after 14 days and after 28 days of immersion. Coupons were cleaned with chromic acid according to ASTM G1-03 standard [10]. Coupons are cleaned once more in an ethanol alcohol bath and air dried before final weight measurements are taken.

4.3 Experimental Work Details (Electrochemical)

Corrosion rate data was gathered using Gamry Instruments Interface 1010E Potentiostat that was connected to a computer. The magnesium alloy is used in a three-electrode system to conduct electrochemical testing [11]. The electrodes used within the system are the sample magnesium alloy as the working electrode, graphite as the counter electrode, and silver calomel electrode as the reference electrode. This system is attached to the Potentiostat through five terminals. A white terminal connects to the reference electrode, a red and orange terminal connects to the counter electrode, a blue and green terminal connect to the working electrode, and a black terminal connects to a proper ground source. Figure [3] below, shows the connection between terminals and the three-electrode system.

Figure [3]: Sample connection between terminals and the three-electrode system.



The electrode system is submerged into simulated body fluid and is set to stabilize for 600 seconds before any test is conducted. Prior to submerging the coupon into the simulated body fluid, it was sequentially sanded down with 400 to 2000 grit sandpaper, washed with ethanol, and dried immediately [12]. After initial preparations, potentiodynamic polarization test was conducted. This testing was conducted on all alloy samples. With the data gathered by the Potentiostat, the Tafel anodic and cathodic slope of the material were measured to determine the corrosion rate.

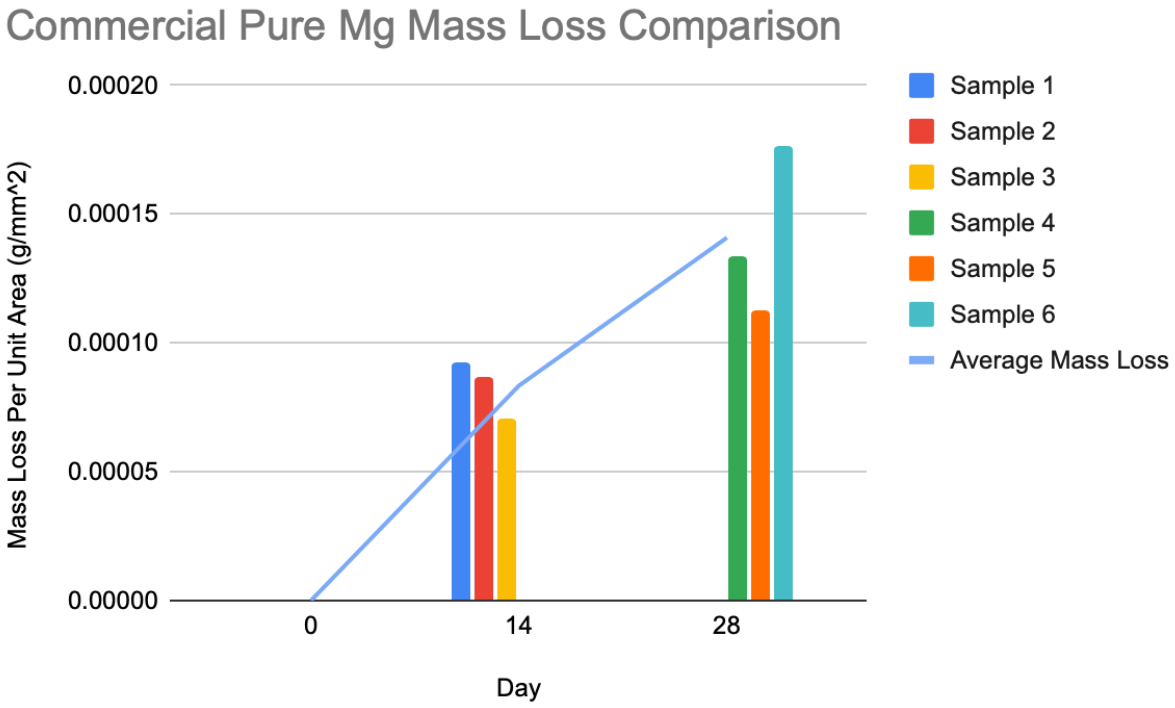
5. Results

5.1 Immersion Testing Results

Figure [4] graphically presents the comparison of the Commercial Pure Magnesium's mass loss over the experimental interval. From the data gathered, it was determined that the average mass loss over a 14-day interval and the 28-day interval was 0.000038 g/mm^2 and 0.000141 g/mm^2

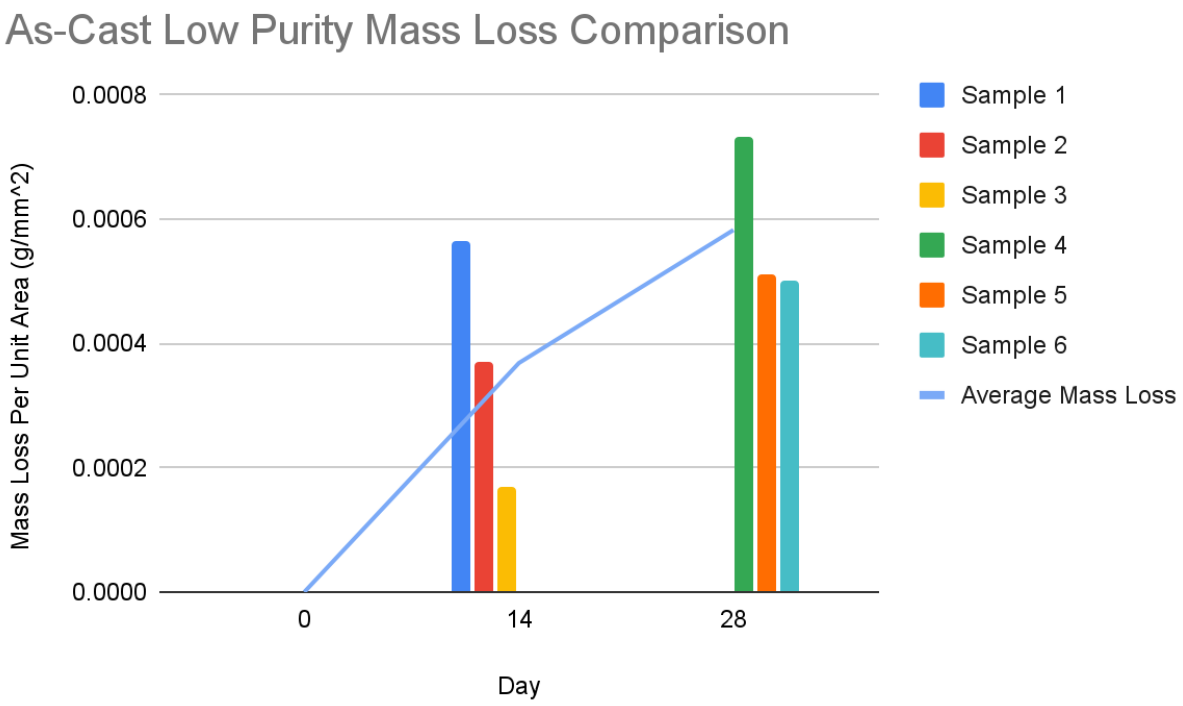
respectively. This means that after 14 days Commercial Pure Magnesium experienced a 6.98% mass loss, and after 28 days it experienced an 11.89% mass loss. The commercial pure mg experiences the “steadiest” mass loss per unit area over the given experimental interval

Figure [4]: Comparison of Commercial Pure Magnesium mass loss over experimental interval.



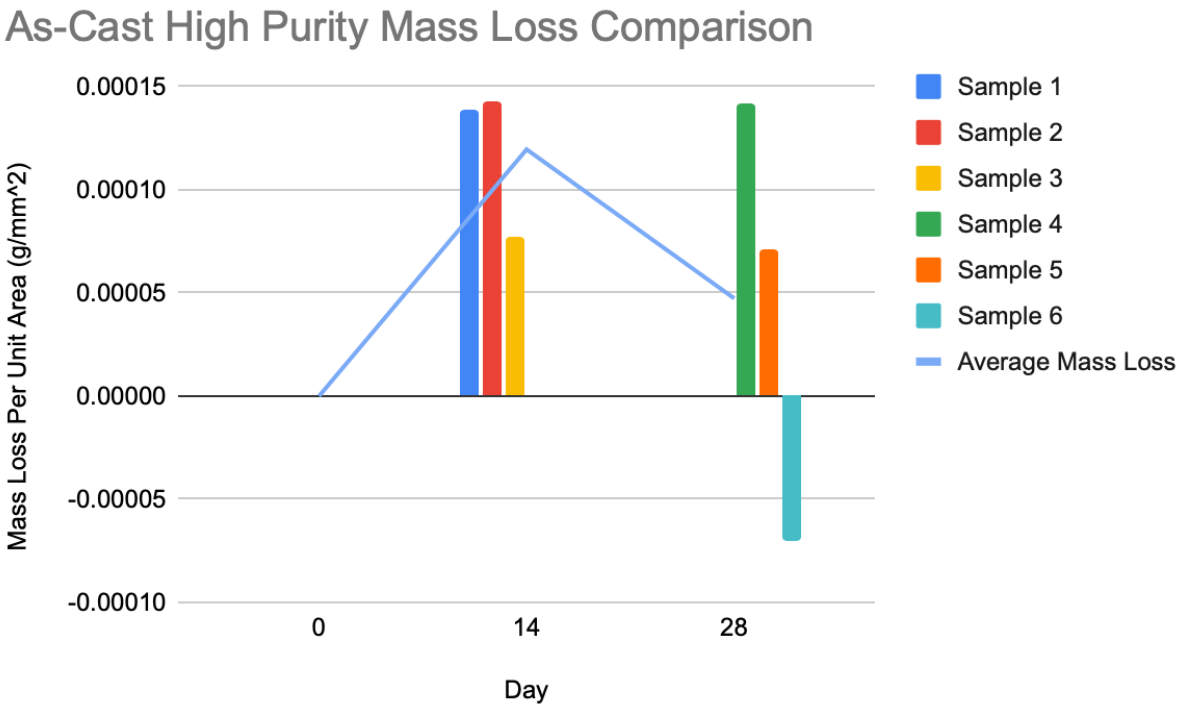
Figures [5] graphically presents the comparison of the As-Cast Low Purity’s mass loss over the experimental interval. The As-Cast Low Purity sample had an average mass loss for the 14-day interval and the 28-day interval of 0.00037 g/mm^2 and 0.00058 g/mm^2 respectively. After 14 days As-Cast Low Purity experienced a 29.97% mass loss, and after 28 days it experienced an 48.55% mass loss This is more consistent, there is an increase of mass loss per unit area over the experimental interval.

Figure [5]: Comparison of As-Cast Low Purity mass loss over experimental interval



Figures [6] graphically presents the comparison of the As-Cast High Purity's mass loss over the experimental interval. The As-Cast Low Purity sample had an average mass loss for the 14-day interval and the 28-day interval of 0.00138 g/mm^2 and 0.00136 g/mm^2 respectively. After 14 days As-Cast High Purity experienced an 8.65% mass loss, and after 28 days it experienced an 3.49% mass loss The samples might have developed a protective coating over time which could explain the "mass gain per unit area" and the decrease in mass loss.

Figure [6]: Comparison of As-Cast High Purity mass loss over experimental interval



Figures [7] graphically presents the comparison of the Hot Rolled High Purity's mass loss over the experimental interval. The Hot Rolled HighPurity sample had an average mass loss for the 14-day interval and the 28-day interval of 0.00141 g/mm^2 and 0.00127 g/mm^2 respectively. After 14 days Hot Rolled High Purity experienced a 11.699% mass loss, and after 28 days it experienced an 3.73% mass loss Like As-Cast High Purity, the samples might have developed a protective coating over time which could explain the "mass gain per unit area" and the decrease in mass loss.

Figure [7]: Comparison of Hot Rolled High Purity mass loss over experimental interval

Figure [8] graphically compares the mass loss over experimental interval of all four samples.

Based on the graph, as-cast low purity samples has the highest corrosion rates.

Figure [8]: Comparison of all four samples' mass loss over experimental interval

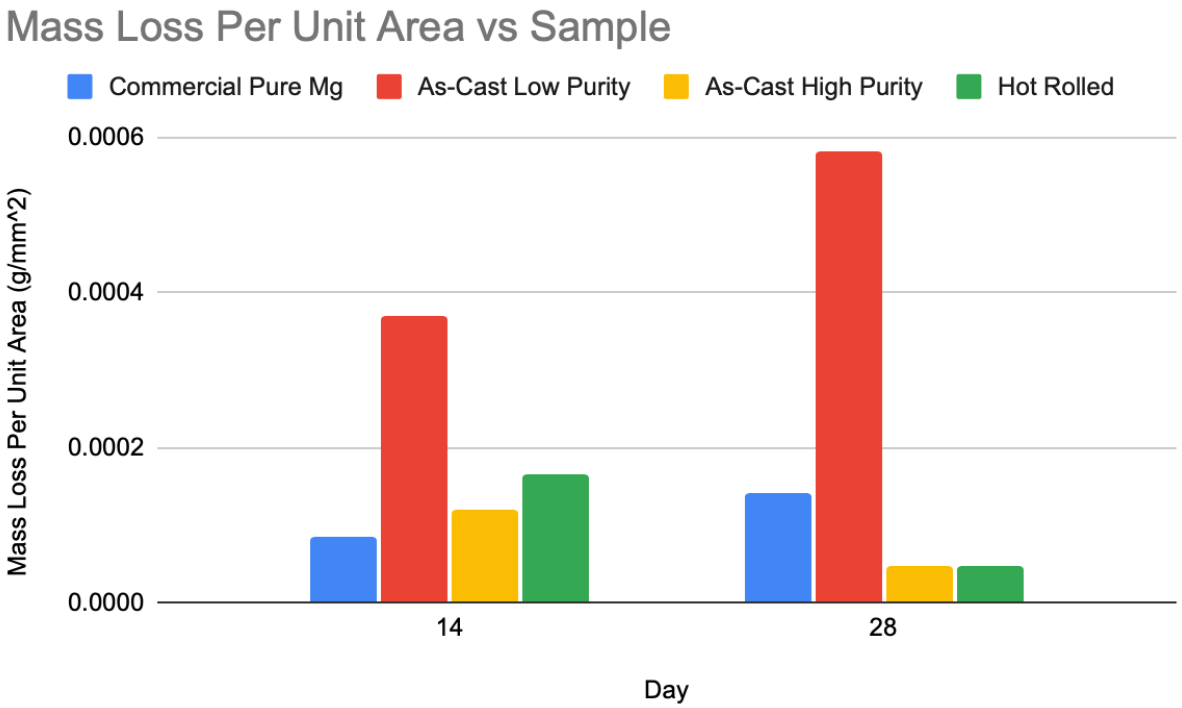
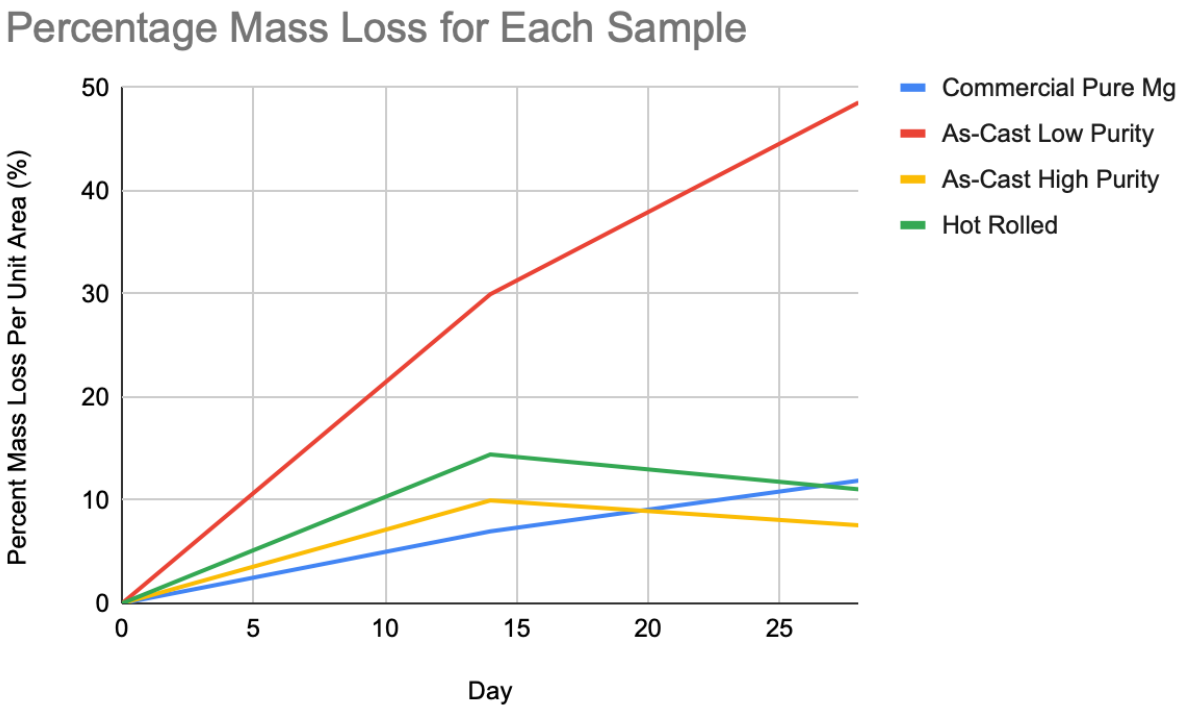


Figure [9], graphically represents, the percent mass loss of each alloy type over given interval based on immersion testing. The as-cast low purity samples have the highest corrosion rates. Meanwhile, the hot-rolled and as-cast high purity showed corrosion rates like that of commercial pure Mg, which is a significant enhancement in the corrosion properties.

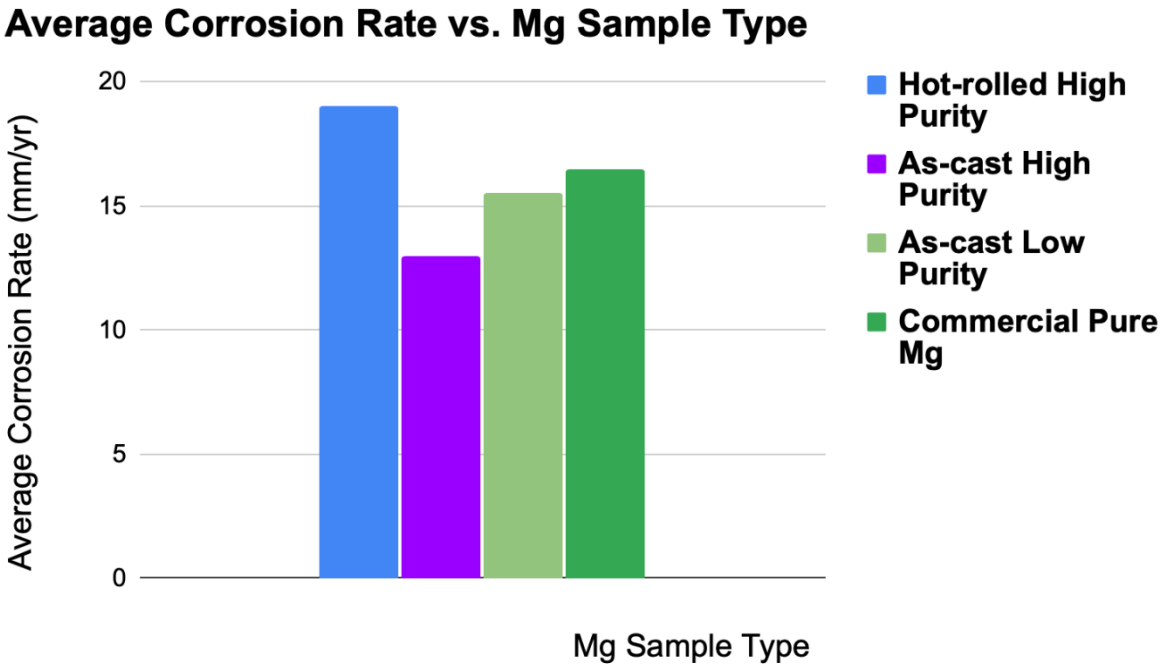
Figure [9]: Comparison of mass loss percentage of all samples over experimental interval



5.2 Electrochemical Testing Results

Figure 10 compares, graphically, the corrosion rate of each alloy types based on electrochemical testing. Similarly, the high purity showed superior corrosion resistance compared to the other tested groups, represented in its lowest corrosion rate. Interestingly, the hot-rolled alloy showed higher corrosion rates than the as-cast alloy, which contradicts with the immersion test results.

Figure [10]: Comparison of corrosion rates of all samples based on electrochemical testing



5.3 Results Comparatively

Table 3 presents the corrosion data gathered through electrochemical and immersion testing. Referring to the first hypothesis, it was hypothesized that when comparing to different purity levels the alloy with the highest purity would demonstrate slower corrosion rates. (meaning as-cast high purity would have slower corrosion rates compared to as cast low purity) As you can see, As-Cast high purity demonstrated lower corrosion rates compared to As-Cast low purity in both immersion testing and in electrochemical testing. Referring to the second hypothesis, it was hypothesized that when comparing to different manufacturing methods, the alloy manufactured using a thermochemical process would demonstrate slower corrosion rates (meaning hot rolled high purity would have slower corrosion rates compared to as-cast high purity) As you can see, based on immersion testing, Hot rolled did in fact have a slower corrosion rate. Based on electrochemical As-cast high purity had a slower corrosion rate. So electrochemical testing

proved our testing to be false, but immersion testing provides more reliable corrosion data results.

Table 3: Corrosion Data gathered through Electrochemical and Immersion testing

Type	Corrosion Current Density (icoor)	Corrosion Rate based on equation mm/yr	Immersion Test Corrosion Rate g/cm^2	
			14 days	28 days
Hot Rolled High Purity	0.00044	19.0458	0.0165	0.0047
As-Cast High Purity	0.00037	12.9789	0.0120	0.0047
As-Cast Low Purity	0.00057	15.521	0.0369	0.0583
Commercial Pure Magnesium	0.00066	16.49	0.0083	0.0141

6. Conclusion

It was hypothesized that when comparing two magnesium-based alloys fabricated using different levels of purity, the high purity alloy would demonstrate slower corrosion rate. Based on electrochemical testing and immersion testing, the hypothesis was proven to be true. It was also hypothesized that an alloy fabricated with a thermomechanical process would show slower corrosion rates than the as-cast ones. Based on electrochemical testing, this was proven to be false. Based on immersion testing, this was proven to be true, which provides more reliable data for corrosion rates. Immersion is more reliable because the corrosion is analyzed and monitored daily. Electrochemical is an extrapolation which is a fast prediction. In the tafel curve, an error can be made when calculating current density (i.e., human error). PDP test is accelerated and

does not count for corrosion products formed on surface and how it can slow the degradation rate after a few days. Data gathered aided in assessing corrosion rates of differently fabricated magnesium- based alloys. Further experiments should be conducted to determine the most desirable magnesium-based alloy fabrication.

7. Acknowledgments

I would like to acknowledge the use of technological, computational, machine, and human resources provides by the University of Tennessee at Chattanooga. Additionally, Dr. Hamdy Ibrahim for his guidance and patience during the whole process. I would like to acknowledge my fellow research partner, Shelby Hash, who has been very helpful and supportive throughout the extent of the experimental work. Additional thanks to Dr. Mohammad Mahtabi for his presence as an additional examiner. Additional thanks to the resources provided by Ben Swords, Andrea James, Dr. Harris Bradley, and many other. Without such tremendous support this thesis would not be possible.

8. References

1. Ibrahim, H., et al., *Resorbable bone fixation alloys, forming, and post-fabrication treatments.* Materials Science and Engineering: C, 2017. **70**: p. 870-888.

2. Qin, Y., et al., *Additive manufacturing of biodegradable metals: Current research status and future perspectives.* Acta Biomaterialia, 2019. **98**: p. 3-22.

3. Prakasam, M., et al., *Biodegradable materials and metallic implants—a review*. Journal of functional biomaterials, 2017. **8**(4): p. 44.

4. Kirkland, N.T. and N. Birbilis, *Magnesium Biomaterials: Design, Testing, and Best Practice*. 2014: Springer.

5. Ibrahim, H., et al., *Effect of Zn content and aging temperature on the in-vitro properties of heat-treated and Ca/P ceramic-coated Mg-0.5% Ca-x% Zn alloys.* Materials Science and Engineering: C, 2019. **103**: p. 109700.

6. Ibrahim, H., M. Elahinia, and H.D. Dean, *Process to produce high-strength and corrosion resistant alloy for patient-specific bioresorbable bone fixation implants and hardware*. 2019, Google Patents.

7. Abdalla, M., et al., *Corrosion Modeling of Magnesium and Its Alloys for Biomedical Applications.* Corrosion and Materials Degradation, 2020. **1**(2): p. 219-248.

8. Instruments, G., *Basics of electrochemical impedance spectroscopy.* G. Instruments, Complex impedance in Corrosion, 2007: p. 1-30.

9. N. Kirkland, N. Birbilis, M. Staiger, Assessing the corrosion of biodegradable magnesium implants: a critical review of current methodologies and their limitations, Acta biomaterialia 8(3) (2012) 925-936

10. A. International, Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens. G1-03, Annual book of ASTM standards 03.02 (2017).

11. Kannan, M. B. (2012). "Enhancing the performance of calcium phosphate coating on a magnesium alloy for bioimplant applications." Materials Letters **76**: 109-112.

12. Torbati-Sarraf, H., et al. (2019). "Electrochemical behavior of a magnesium ZK60 alloy processed by high-pressure torsion." Corrosion Science **154**: 90-100.