An assessment of magnesium AZ31 coronary stents manufacture

Mariana Nuñez-Nava¹², Elisa Vazquez¹², Wendy Ortega-Lara¹, Ciro A Rodriguez¹² and Erika García-López¹²

¹ Tecnológico de Monterrey, Escuela de Ingeniería y Ciencias, Ave. Eugenio Garza Sada 2301 Sur, Monterrey, N.L., 64849, Mexico
² Laboratorio Nacional de Manufactura Aditiva y Digital MADiT, Apodaca, Nuevo León, 66628, Mexico
E-mail: garcia.erika@tec.mx

Keywords: AZ31 magnesium alloy, PCL, dynamic degradation, acid pickling, laser cutting

Abstract
AZ31 magnesium coronary stents were studied through a manufacturing process chain involving laser cutting, acid pickling, and dip coating. The purpose of this study was to evaluate surface thickness and geometrical dimensions of stents after processing. Stents were dip coated in a solution using PCL with 1% of TiO2. Additionally, AZ31 coronary stents were dynamically tested using a degradation system based on peristaltic pumps. Our results indicate that coated stents degraded slower than AZ31 uncoated control stents. After 4 weeks of dynamic degradation under flowing Hank’s solution, coated stents lost only ~9% in weight while uncoated stents lost ~27% in weight. Stents were qualitatively evaluated after four weeks of degradation. Our results demonstrate the formation of micro-pores after one and two weeks of degradation for coated stents. Lamination was observed after three weeks of degradation, meanwhile, uncoated stents resulted with notches and an irregular surface caused by degradation.

1. Introduction

Biodegradable coronary stents have several specifications (i.e., wider struts, greater stent thickness, lower degradation rate, higher radiolucent properties, and lower corrosion rate) to accomplish stent application requirements. Coronary stents have chronic complications during placement related to restenosis and thrombosis [1]. Therefore, a second intervention must be performed to allow blood flow into the artery [2, 3]. Magnesium alloys have been mainly evaluated as a solution for stent replacement due to their corrosion mechanism that allows dissolving the alloy components in blood. Among the variety of magnesium alloys, WE43 and AZ31 alloys have the lowest corrosion rate; 6.82 and 10.08 mm year−1, respectively [4–6]. This is promising when stent durability is a major concern. The corrosion rate of WE43 and AZ31 alloys can vary between 90 d and 4 months depending on the alloying additives and coatings [7]. Magnesium coronary stents are manufactured in a sequence of fabrication processes: laser cutting, acid pickling, sterilization and coating. Laser cutting on magnesium alloys has been studied with considerably good results in reducing surface roughness, dross, slag, and thermal effects [8]. It is of great importance to have a clean surface free of melted particles to accomplish a worthy interface between the coating and the stent’s metallic surface. The most common chemical cleaning methods for magnesium alloys are vapor degreasing, solvent cleaning, emulsion cleaning, alkaline cleaning, and acid pickling. Acid pickling baths fulfills important functions to reduce dross particles, slag, or surface contamination in magnesium alloys. These functions are related with removing corrosion, eliminating oxide films and providing a clean surface that is receptive to chemical-conversion coating [9]. Additionally, polymeric coatings have come up as a solution to increase the lifetime of the medical device and to create a protective barrier [10]. Although there is a variety of coating techniques for stent coverings (dip coating, electro-treated coating, plasma coating and spray coating) [11], dip coating is the simplest method to cover medical devices compared to other methods [12]. This technique consists of depositing uniform layers at a controlled speed and quantity of cycles. Some dip coated commercial coronary stents are CypherTM stent (Cordis, US), BiodivYsioTM (Biocompatibles Ltd UK), ZoMaxxTM (Abbott Vascular, US) and Endeavor (Medtronic Inc., US)
Table 1. Literature review of acid pickling and coatings in AZ31 alloy.

| References | Magnesium alloy / coating method (Geometry) | Chemical etchant solution | Immersion time in chemical etchant (s) | Coating solution | Response |
|------------|------------------------------------------|---------------------------|----------------------------------------|------------------|----------|
| [21]       | AZ31 (sheets; length: 50 mm, width: 50 mm, thickness: 2 mm) | $\text{H}_2\text{SO}_4$ (Conc g l$^{-1}$) (10–50) + DI water | 15, 30, 60, 120 | None | – Material removed |
|            |                                           | $\text{HNO}_3$ (20–80) + DI water |                                      |                  |          |
|            |                                           | $\text{H}_2\text{PO}_4$ (40–80) + DI water |                                      |                  |          |
| [20]       | AZ31 (sheets; length: 50 mm, width: 50 mm, thickness: 2 mm) | $\text{Acetic acid CH}_3\text{COOH} + \text{Calcium nitrate Ca(NO}_3\text{_2} (100–300,50)$ | 15, 30, 60, 120 | None | – Surface roughness |
|            |                                           | $\text{Oxalic acid, C}_2\text{H}_2\text{O}_4\text{H}_2\text{O} (20–80)$ |                                      |                  |          |
|            |                                           | $\text{Citric acid, C}_6\text{H}_8\text{O}_7 (40–120)$ |                                      |                  |          |
| [23]       | MgZnMn/evaporation of organic coatings (strips; length = 15 mm, width = 5 mm, thickness 1.5 mm) | –Mechanical polishing | None | poly(trimethylene carbonate) (PTMC) and Poly($\varepsilon$-caprolactone) (PCL) | – Magnesium ion released |
|            |                                           |                            |                                      |                  |          |
| [24]       | AZ31/Dip coating (disks; Diameter: 2 cm, coating thickness: 53 μm ) | $\text{H}_2\text{O}$ | 900 | PropytriEthoxySilane (APTES), AminoPropyl TriMethoxySilane (GPTMS), Tris (TriMethylSilyl) Phosphate (TMSPh). | – Coating morphology |
| [22]       | AZ31 (tube; diameter: 2.5 mm, thickness: 0.2 mm) | $\text{HNO}_3$ + 90% ethanol | 5–600 | None | – Corrosion properties |
|            |                                           |                            |                                      |                  |          |
| [27]       | AZ31 / (thin sheets; thickness: 0.4 mm, tube; diameter: 2.5 mm and thickness: 0.2 mm) | $\text{HNO}_3$ + 95% ethanol | 10–180 | None | – Thickness reduction |
| [15]       | AZ31/dip coating (tube; diameter = 10 mm, thickness = 0.2 mm) | –none | None | Poly($\varepsilon$-caprolactone) (PCL) and poly(trimethylene carbonate) (PTMC). | – Kerf width |
|            |                                           |                            |                                      |                  |          |
Several works have studied the effect of acid pickling adding nanoparticles. Table 1 presents a literature review of acid pickling and coatings in the AZ31 alloy per year.

### Table 1. Chemical composition of AZ31 minitubes.

| C(%) | OD = 1.8 mm | OD = 1.8 mm | OD = 3 mm | OD = 3 mm |
|------|-------------|-------------|------------|------------|
| Al   | 2.819       | 2.609       | 3.112      | 2.5        |
| Ca   | 0.035       | 0.039       | 0.036      | 0.04       |
| Cu   | 0.0034      | 0.0017      | 0.0009     | 0.05       |
| Fe   | 0.012       | 0.014       | 0.01       | 0.005      |
| Mg   | Balance     |             |            |            |
| Mn   | 0.016       | 0.016       | 0.016      | 0.2        |
| Si   | <0.001      | <0.001      | <0.001     | 0.005      |
| Zn   | 1.082       | 1.023       | 1.359      | 0.2        |

[13] Several studies have worked on controlling the localized corrosion in magnesium alloys through adding rare earth and metallic elements such as lithium, zirconium and calcium in their basic chemical composition [10]. However, polymeric coatings have offered tremendous opportunities in terms of drug loading and control over drug release kinetics [14]. Particularly, Polycaprolactone (PCL) polymer has a lower degradation rate than magnesium alloys [15] which preserves the surface’s integrity of coated stents. Additionally, the incorporation of nanoparticles with a drug eluting purpose led to create multifunctional coatings [16–18]. Tamjid et al [19], performed a drug release study using PCL as polymer matrix and TiO2 nanoparticles in 2D films. They used diverse concentrations of tetra-cycline hydrochloride (TCH) as an antimicrobial agent. Their study demonstrates that almost all the drug was released within almost 10 h incubation for PCL films. While, the PCL/TiO2 film released around 50% of the TCH after 10 h of incubation which demonstrated the advantages of adding nanoparticles. Table 1 presents a literature review of acid pickling and coatings in the AZ31 alloy per year. Several works have studied the effect of acid pickling [20–22] and coating [15, 23] on magnesium materials (i.e. tubes, sheets, rods or disks as raw material). For example, Brusciotti et al [24] evaluated AZ31 disks after being etched and coated with results on surface degradation. In this study, we studied the processing stages (laser cutting, acid pickling, coating and degradation response) to manufacture coronary stents which have geometrical and surface implications due to the micro-size scale of their complex geometry. Additionally, the dynamic degradation response of biodegradable coronary stents due to their corrosion mechanism caused by fluid is of great interest in magnesium alloys. Biodegradable metallic materials have been studied in order to analyze the degradation rate in similar conditions to those in the human body [3, 25, 26]. For example, Lévesque et al performed a test bench to approximate physiological conditions of coronary arteries in order to study the corrosion mechanisms of magnesium alloys [3]. In this study, AZ31 magnesium coronary stents process chain was investigated. Stents were laser cut and cleaned using the acid pickling method. Additionally, they were dip coated with a PCL and TiO2 solution and degraded using a dynamic system for four weeks. In the study reported here, the main objective was to evaluate the influence of the process’ sequence and their parameters in the stent’s quality to simulate the stent performance in similar conditions to those in the human body. Based on the literature review, the contribution of this study is related to the analysis of etching and coating of coronary stents compared with raw geometries such as disks, tubes or sheets.

### 2. Materials and Methods

#### 2.1. Magnesium minitubes

Chemical composition of the different raw tube material is shown in Table 2. Tubes were acquired with different suppliers. The chemical composition of the tubes with OD of 3 mm and a thickness of 0.25 mm was provided by the supplier (Complex Materials, Eindhoven, Netherlands). While other tubes (OD = 3 mm, T = 0.22 mm; OD = 1.8 mm T = 0.16 mm; OD = 1.8 mm T = 0.11 mm), were bought from Yangzhou Sanming Medical Supply (Yangzhou, Jiangsu, China) and their chemical composition was obtained using atomic absorption spectroscopy (Laboratorios Fairchild, NL, Mexico) based on ASTM E1024-97. Table 2 presents the chemical composition by material used in experimental trials.

#### 2.2. Laser cutting

A fiber laser source (YLR/150/1500, IPG photonics, USA) adapted with a fiber core with a diameter of 50 μm, a 120-mm collimator, and a 50-mm focal lens was used for experimental trials. A theoretical spot size of 21 μm.
was obtained with this configuration. AZ31 minitubes with different outer diameters and thicknesses were laser cut using a high-density polyethylene drape mounted on an acrylic to contain argon and create an inert atmosphere. The chamber set up is explained in our previous work [8]. The tubes were laser cut until an oxygen sensor InPro 6850I (Mettler Toledo, Cd. de Mexico, Mexico) ensuring an oxygen level inside the chamber below 5%. The geometry cut was Palmaz-Schatz stent design [28]. Table 3 presents the applied cutting parameters used for each minitube. Parameters highlighted correspond to our calculations of spot overlap and pulse energy based on our previous work.

### 2.3. Acid pickling

AZ31 magnesium stents were cleaned with a 70% ethanol/distilled water solution in an ultrasonic bath during 5 min. The acid pickling technique was used to remove slag and dross particles caused by metal fusion in laser cutting with the main objective to reduce surface roughness on the cutting edge. The etchant solution consisted of 10 ml HNO3 and 90 ml of ethanol. Stents were submerged in time intervals

Intervals were selected based on preliminary tests before pitting corrosion was observed. Samples were washed using the same ethanol/distilled water solution and dried with compressed air.

### 2.4. Dip coating

Eight coronary stents were laser cut, acid pickled then coated. Twenty-four measurements were performed per stent to evaluate thickness. Coronary coated stents were placed in an extraction hood and in a vacuum desiccator to eliminate moisture. Samples were sterilized using a low temperature gas plasma sterilizer (Sterrad, ASP, CA, USA) for 47 min. The polymer solution was made of PCL (Poly(caprolactone) (MW 80,000, Aldrich, St. Louis, MO, USA)) with 1% of TiO2 (>99.5%, Sigma-Aldrich, MO, USA) and 90% of CCl4 as solvent (Chloroform 98%, Sigma-Aldrich, MO, USA).

Solution was stirred during 4 h at 250 RPM to dissolve the polymer. A dip coated machine was built using a linear guide with a Z resolution of 10 μm and based on a stepper motor actuation. It was programmed using an Arduino card to set the entry and withdrawal speed of 125 mm min⁻¹. Stents were fully dip coated in PCL with 1% of TiO2 solution in a vertical position during 5 seconds per cycle and for 10 cycles to allow surface wetting. Samples were suspended with a clip and were dried during 10 min at 70 °C per cycle using a 50 w GU10 halogen lamp (Philips, Eindhoven, Netherlands). Specimens were maintained in a desiccator at room temperature. Coated stents were weighed using an Explorer scale (OHAUS, Cd. de Mexico, Mexico). Figure 1 presents the stages (start up, deposition, drainage, and drying) for surface coating. In stent immersion (figure 1(a)), the stent is placed in solution; in the start-up phase (figure 1(b)), the substrate is completely wetted; in deposition (figure 1(c)), a thin film is deposited on the stent and then the excess of solution is eliminated during drainage in the drying stage (figure 1(d)), to evaporate the solvent with an incandescent lamp (figure 1(e)).

### 2.5. Coating characterization

Characterization of the PCL solution with TiO2 was performed using a XRD (x-ray powder diffraction) technique to evaluate the crystallinity of the nanoparticles composite. XRD was assessed between 10° and 85° within a 2θ range, and a step size of 0.026. The equipment used was a Panalytical Empyrean diffractometer (Panalytical, Almelo, The Netherlands), and a CuKα radiation, of which the wavelength was λ = 1.5406 Å. The voltage and current applied were 45 kV, and 40 mA, respectively. Infrared studies were developed with Fourier transform infrared (FTIR) (Perkin Elmer, MA, USA) model Spectrum 400 recorded in the wavenumber range of 4000–400 cm⁻¹ at room conditions.
2.6. Dynamic degradation

A dynamic degradation system was built using four peristaltic pumps. An Arduino microcontroller and a 4-motor driver were used to control the flow rate. Pumps were mounted on a metal frame and were cleaned using a 70% ethanol and distilled water solution during 15 min before testing. Hank’s solution was poured in a recipient by each stent and kept at 37 °C using a hot plate while pH was maintained at 7.4, to simulate physiological conditions. The solution was recirculating using a flow rate of 40 ml min⁻¹ to simulate blood flow [29, 30]. Stents were maintained inside a hose while the solution was pumped. Figure 2 presents the dynamic degradation system used for experimental trials. Figure 2(a) presents the recirculating flow system and figure 2(b) shows the dynamic degradation system. Temperature and pH measurements were obtained every 24 h using a pH meter HI2213 (Hanna Instruments, RI, USA). Once the pH value reached 7.4, Hank’s solution...
was changed to control the biochemical reactions of degradable magnesium. Dynamic corrosion tests were performed in a total of 12 stents (8 stents were coated with the same conditions and 4 stents were left as control without coating). Coated stents were evaluated per pair to have a replicate. Weight loss ($W_L$) was calculated using the next formula:

$$W_L = \frac{w_f - w_i}{w_i} \times 100\%$$

where $w_f$ and $w_i$ are the final and initial weight of the stents, before and after dynamic corrosion tests.

2.7. Coronary stent characterization

Surface roughness and tube thickness were measured on the cutting edge and on the coronary stent’s surface using an Infinite Focus Variation microscope (Alicona, USA) with a vertical resolution of 0.1 μm, a lateral resolution of 2 μm and a 20× objective lens after acid pickling. Additionally, surface quality was characterized after acid pickling, dip coating, and degradation using a scanning electron microscopy (SEM) model EVO MA25 (Zeiss, Oberkochen, Germany). These images were analyzed using the ImageJ software (NIH, MD USA).

Figure 3 presents the surface roughness characterization. For laser cutting and acid pickling the surface roughness was measured on the cutting edge to evaluate the topography. After stents were coated, surface roughness was measured on the stent’s surface (lateral roughness).

3. Results and discussion

3.1. Laser cutting & acid pickling

Figure 4 illustrates the coronary stents after laser cutting (a), (c), (e), (g). Hence, some defects are observed after laser cutting, for example dross particles (a), (g), adhered particles on the stent’s surface (c) and irregularly cut edges (e). Once coronary stents were pickled, etched stents show a cleaner surface (b), (d), (f), (h). However, samples of figures 4(d), (f), (h) have cleaner edges compared with figure 4(b). The average surface roughness of samples after laser cutting was measured to compare it with etched samples. Tubes with thicknesses of 0.25 mm resulted with a higher average surface roughness (~1.47 μm) than other samples (~0.47–0.54 μm). The cutting parameters of tube samples with lower surface roughness were previously studied [8]. Further experiments must
be performed to minimize surface roughness in tubes with a thickness of 0.25 mm. Additionally, this tube has less content of Zinc compared to other tubes. When the addition of Zinc is greater than 1% it makes the alloy prone to hone cracking and its corrosion resistance can be improved [9].

Figure 3 illustrates the average surface roughness results after stents were acid pickled. Stents with thicknesses of 0.11 mm and 0.16 mm resulted with a cleaning time of 180 s. For stents with a thickness of 0.16 mm, when time was increased, surface roughness rose. It is attributed to some located pitting corrosion on the cutting edge caused by an overexposure to acid solution. Power models were adjusted in experimental tests and R2 values are illustrated in Figure 5. Minimum values of average surface roughness were in between 0.26 and 0.34 μm. Plasma etching has been presented as a method to improve surface roughness in magnesium, resulting in a 10% reduction (from 0.191 to 0.172 μm) compared with chemical etching (i.e., phosphoric acid etchant).
Demir et al reported surface roughness values ($R_a$) of 0.56 $\mu$m and 0.62 $\mu$m after chemical etching when a CW and femtosecond pulsed laser source are used, respectively [27]. Additionally, Zhou et al, presented a study of biological efficiency in vascular implants based on surface texturing gradients [32]. Their results revealed the importance of the role of surface topography in Magnesium materials which have an influence on cell activity. Further experiments can be performed to evaluate cell activity in coronary stents manufactured with different processing parameters. Figure 6 illustrates the thickness evaluation of coronary stents after acid pickling.

Thickness reduction in the stent’s cutting edge did not follow a trend. However, an experiment was kept until an abrupt thickness reduction change appeared. For stents with a thickness of 0.16 mm, a reduction change from 3.6 $\mu$m to 13.2 $\mu$m when etching time is in between 150s to 180 s (8% of the thickness) was observed. For stents with a thickness of 0.11 mm, surface roughness (figure 5) was not evaluated after 180 s, due to an increase in thickness reduction from 1.1 $\mu$m to 12.5 $\mu$m (i.e., 11.5% of the thickness). Stents with thicknesses of 0.22 mm and 0.25 mm required a cleaning time of 240 s to reduce surface roughness on the cutting edge. For stents with thicknesses of 0.22 mm, a maximum reduction of 7.2% of the thickness was obtained after 240 s of acid pickling. Meanwhile, stents with thicknesses of 0.25 mm, a reduction of 13% was found. The etching time differences
between tubes with an OD of 3 mm and a thickness of 0.25 mm and other tubes can be attributed to surface roughness obtained after laser cutting and the chemical composition.

3.2. Coating characterization

XRD results are shown in figure 7, in diffractogram (figure 7(a)), the peaks presented are similar to titanium dioxide, the phases observed are a mix of anatase and rutile principal intensities, (27.4°, 54.3°, 36.07°), and (25.26°, 47.9°, 37.81°), respectively. Figure 7(b) presents the characteristic behaviour of a polymer with a certain percentage of the crystalline phase. Intense and broad peaks are presented at 21.3° and 23.7°, a bump is developed between 16° and 27° indicating a low crystallinity. Figure 7(c) show the combination of more intense peaks for PCL and TiO₂ (both phases, anatase, and rutile). Infrared analysis is shown in figure 8. Spectra of figures 8(a) and (b) show similar bands in the range of 4000–400 cm⁻¹. In both spectra, asymmetric and symmetric CH₂ stretching of around 2937 and 2867 cm⁻¹. At, 1723 and 727 cm⁻¹ bands of carbonyl stretching appeared. Multiple peaks are related to C-O, C-C stretching vibrations, and C-O-C asymmetric stretching, 1293, 1240 cm⁻¹. Bands of O–C–O stretching and symmetric C–O–C stretching at 1190 and 1160, respectively. In figure 8(b), new bands are displayed at 1577 cm⁻¹ associated with carboxylic vibrations coordinated with
titanium. Two shoulders appear at 862 and 642 cm$^{-1}$ related with the anatase phase presence. Additionally, a Ti–O rutile shoulder is located at 447 cm$^{-1}$.

3.3. Dip coating

Coronary stents with an outer diameter of 3 mm and a thickness of 0.25 mm were coated. Figure 9 presents the stent thickness evaluation of eight stents after acid pickling and dip coating. The error bars represent the standard error of 24 measurements. The number of measurements were quantified per stent due to the variations presented in each coated sample. The raw material has an inherent thickness variation due to the extrusion process ($\pm 25 \mu m$). The deviations of coated stents are explained by the stent’s proposed geometry. H-strut geometry promotes metal zones to cause conglomerations compared to hollow spaces where less material is deposited per cycle. It causes an irregular cross section of the stent. Lateral surface roughness was quantified and reported in figure 10. Coated stents showed variation among measurements of average surface roughness ($R_a$). When a stent was coated, small porosities were formed on the surface which increased both surface roughness parameters which, resulted in $\sim 1.5 \mu m$ and $\sim 10 \mu m$ for an average surface roughness ($R_a$) and a ten point mean roughness ($R_z$), respectively. Several studies have analyzed the influence of laser and etching parameters on surface roughness [8, 22]. However, results are not conclusive for coated stents. According to Ping Li et al, the degree of roughness and the magnesium alloy composition can promote
degradation which leads to osmotic stress for cells [33]. Further experiments can be performed to evaluate the influence of surface roughness in a biological response.

3.4. Dynamic degradation

The weight of the stents was monitored after acid pickling, PCL coating and degradation. Figure 11 presents the weight loss percentage per week of degradation with power models adjusted and pH average measurements. AZ31 magnesium alloy without coating was used as control. From results obtained, AZ31 uncoated alloy presents a weight loss percentage of around 27% after four weeks of degradation while stents coated with PCL and TiO2 presents a weight loss percentage of around 9%. For AZ31 coated with PCL and TiO2, pH was effectively monitored and controlled below 7.4.

Figure 12 presents a qualitative study of the degraded stents. Coated stents without degradation (figures 12(a), (d), (g), and (j)) were performed with the same dip coated conditions. In deposition stage, the PCL with TiO2 film was deposited. However, in the drainage stage, a meniscus formation at the end of the stent (red oval) was observed. This meniscus was observed in the H– strut geometry. Although stents were fully coated laterally, it presented a non-uniform thickness. Figures 12(b), (c), (e), (f), (h), (i), (k), (l) present stents after weeks 1, 2, 3, and 4 of degradation, respectively. Additionally, the degraded stent images (figures 12(c), (f), (i), (j)) are a zoom in of degraded stent. After weeks 1 and 2 some pores are observed (figures 12(b), (c), (e), (f)) while after weeks 3 and 4 polymer lamination is observed (figures 12(h), (i), (k), (l)). The usual degradation process in AZ31 alloys is proposed by Hanas et al [34], PCL allows a more controlled degradation, however it degrades over time by hydrolysis of ester bonds and leads to fatal cracks and pitting. The pores observed on the surface after weeks 1 and 2 of degradation have a diameter of ∼3.1 μm while after the second week they presented a pore diameter of ∼9.8 μm. This phenomenon was explained by Chen et al, they found that hydrogen escapes from high purity magnesium surfaces and pushes away the polymer (i.e., PCL and PLA) coatings which causes the polymer’s degradation [17].

Additionally, Catauro et al, performed polymeric coatings of 5 and 10 wt% PCL with TiO2 in titanium disks which presented pores promoting cellular growth [26]. These pores have a diameter of ∼4 μm after 16 weeks which can be compared with our results that show the same results in only 3 weeks. The accelerated degradation in our results can be explained due to the flow rate used in the dynamic degradation system which represents an increase of almost 30.5 times (1.35 ml min \(^{-1}\) versus 40 ml min \(^{-1}\)).

Figure 13(a)–(d) shows the degradation process in uncoated stents. Figure 13(a), (b) presents the stent after one week of degradation and figures 13(c), (d) illustrates the stent’s surface after four weeks of degradation. At the end of the corrosion period cracks and notches were developed. According to Ostrowski et al PCL coating showed the least amount of surface corrosion and not visible cracking. [35] Further experiments can be performed to evaluate the incorporation of drugs to coronary stents to promote a slower ion release rate.

![Figure 11](image-url) Weight loss percentage and pH measurements in degraded stents.
4. Conclusions

This study reports all relevant manufacturing steps of coated AZ31 stents and utilizes realistic stent geometry. Conclusions can be summarized as follows:

- A complete process route of AZ31 magnesium coronary stent’s fabrication is presented. The stents were laser cut, acid pickled, coated and evaluated through a dynamic degradation process.

- Acid pickling of stents resulted with the best surface quality with 180 and 240 s of etching time for the smallest (0.11 and 0.16 mm) and largest (0.22 and 0.25 mm) thicknesses, respectively.

- Dip coating technique was used to cover coronary stent surface. Coronary stents were coated with a solution of PCL and TiO₂ polymer.

Figure 12. AZ31 coated coronary stents observed in SEM; coated stents without degradation (a), (d), (g), (j); first week of degradation (b), (c); second week of degradation (e), (f); third week of degradation (h), (i); fourth week of degradation (k), (l).

Figure 13. AZ31 without coating coronary stents without coating; (a), (b) stent after one week of degradation, (c), (d) stent after four weeks of degradation.
The coated AZ31 magnesium stent with PCL + TiO₂ lost 9% of its weight while the uncoated AZ31 magnesium stent lost 27% of its weight after dynamic degradation. Therefore, the stent degradation was delayed, and the use of polymer functionalized surface could be explored in further research.

Acknowledgments

We are grateful to the assistance received from Regina Elizabeth Vargas Mejia. This work has been supported by the Advanced Manufacturing Focus Group of Tecnológico de Monterrey. We are grateful to the assistance received from Regina Elizabeth Vargas Mejia. This work has been supported by

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Elisa Vazquez https://orcid.org/0000-0002-1228-9636
Ciro A Rodriguez https://orcid.org/0000-0003-2289-4239
Erika García-López https://orcid.org/0000-0002-3341-298X

References

[1] Urban P et al 2011 Stent thrombosis and bleeding complications after implantation of sirolimus-eluting coronary stents in an unselected worldwide population surveillance registry Journal of the American College of Cardiology 57 1445–54
[2] Farhatnia Y, Pang J H, Darbishire A, Dee R, Tan A and Seifalian A M 2016 Next generation covered stents made from nanocomposite materials: a complete assessment of uniformity, integrity and biomechanical properties Nanomedicine Nanotechnology, Biol. Med. 12 1–12
[3] Lévesque J, Hermawan H, Dubé D and Mantovani D 2008 Design of a pseudo-physiological test bench specific to the development of biodegradable metallic biomaterials Acta Biomater. 4 284–95
[4] Grogan J A, Leen S B and McHugh P E 2012 Comparing coronary stent material performance on a common geometric platform through simulated bench testing J. Mech. Behav. Biomed. Mater. 12 129–38
[5] Li N, Guo C, Wu Y H, Zheng Y F and Ruan L Q 2012 Comparative study on corrosion behaviour of pure Mg and WE43 alloy in static, stirring and flowing Hank’s solution Corros. Eng. Sci. Technol. 47 346–51
[6] Farì S, Ge Q, Vedani M, Gastaldì G V D, Migliavacca F and Trasatti A 2010 Evaluation of material properties and design requirements for biodegradable magnesium stents Rev. Mater. 15 96–103
[7] Persaud-Sharma D and Mcgrorona D 2012 Biodegradable magnesium alloys: a review of material development and applications Journal of Biomechanics, Biomaterials, and Tissue Engineering 12 26–39
[8] Garcia-López E, Ibarra-Medina J R, Siller H R, Lammel-Lindemann J A and Rodriguez C A 2018 Surface finish and back-wall-dross behavior during the fiber laser cutting of AZ31 magnesium alloy Micromachines 9 885
[9] Mardanian M and Baker H 1999 ASM specialty handbook: magnesium and magnesium alloys 10th edn Materials Park, OH: ASM International
[10] Moravej M and Mantovani D 2011 Biodegradable metals for cardiovascular stent application: Interests and new opportunities Int. J. Mol. Sci. 12 4250–70
[11] Livingston M and Tan A 2016 Coating techniques and release kinetics of drug-eluting stents J. Med. Devices, Trans. ASME 10 1–21
[12] Acharya G and Park K 2006 Mechanisms of controlled drug release from drug-eluting stents Adv. Drug Delivery Rev. 58 387–401
[13] Christos D and Onyeshon I 2011 Novel coating technologies of drug-eluting stents In Studies in Mechanobiology, Tissue Engineering and Biomaterials 8 127–125
[14] Grabon N, Martin D P, Schmitz K P and Sternberg K 2010 Absorbable polymer stent technologies for vascular regeneration J. Chem. Technol. Biotechnol. 85 744–51
[15] Yuan T et al 2016 Fabrication of a delaying biodegradable magnesium alloy-based esophageal stent via coating elastic polymer Materials (Basel) 9 364
[16] Woodruff M A and Hutmacher D W 2010 The return of a forgotten polymer–polycaprolactone in the 21st century Progress in Polymer Science (Oxford) 35 1217–56
[17] Chen Y, Song Y, Zhang S, Li J, Zhao C and Zhang X 2011 Interaction between a high purity magnesium surface and PCL and PLA coatings during dynamic degradation Biomater. 32 6025005
[18] Szott L M, Irvin C A, Trollsas M, Hossainy S and Ratner B D 2016 Blood compatibility assessment of polymers used in drug eluting stent coatings Biointerphases 11 029806
[19] Tamjidi E, Bohtouli M, Mohammadi S, Alipour H and Nikkhah M 2020 Sustainable drug release from highly porous and architecturally engineered composite scaffolds prepared by 3D printing J. Biomed. Mater. Res. A 108 1426–38
[20] Nwaogu U C, Blawert C, Scharnagl N, Dietzel W and Kainer K U 2010 Effects of organic acid pickling on the corrosion resistance of magnesium alloy AZ31 sheet Corros. Sci. 52 2143–54
[21] Nwaogu U C, Blawert C, Scharnagl N, Dietzel W and Kainer K U 2009 Influence of inorganic acid pickling on the corrosion resistance of magnesium alloy AZ31 sheet Corros. Sci. 51 2544–56
[22] Demir A G, Previtali B and Biffi C A 2013 Fibre laser cutting and chemical etching of AZ31 for manufacturing biodegradable stents Adv. Mater. Sci. Eng. 2013 692635

[23] Wang J et al 2013 A surface-eroding poly(1,3-trimethylene carbonate) coating for fully biodegradable magnesium-based stent applications: toward better biofunction, biodegradation and biocompatibility Acta Biomater. 9 8678–89

[24] Brusciotti F, Snihirova D V, Xue H, Montemor M F, Lamaka S V and Ferreira M G S 2013 Hybrid epoxy-silane coatings for improved corrosion protection of Mg alloy Corros. Sci. 67 82–90

[25] Hermawan H, Moravej M, Dubé D, Fiset M and Mantovani D 2007 Degradation behaviour of metallic biomaterials for degradable stents in Advanced Materials Research 15–17 113–8

[26] Catauro M, Papale F and Bollino F 2015 Characterization and biological properties of TiO2/PCL hybrid layers prepared via sol-gel dip coating for surface modification of titanium implants J. Non. Cryst. Solids 415 9–15

[27] Gökhan Demir A and Previtali B 2014 Comparative study of CW, nanosecond- and femtosecond-pulsed laser micromachining of AZ31 magnesium alloy stents Biointerphases 9 029004

[28] Schiavone A, Zhao L G and Abdel-Wahab A A 2014 Effects of material, coating, design and plaque composition on stent deployment inside a stenotic artery - Finite element simulation Mater. Sci. Eng. C 42 479–88

[29] Wang J et al 2014 Flow-induced corrosion behavior of absorbable magnesium-based stents Acta Biomater. 10 5213–23

[30] Frattolin J et al 2016 Development of a novel biodegradable metallic stent based on microgalvanic effect Ann. Biomed. Eng. 44 404–18

[31] Galvin E, Morshed M M, Cummins C, Daniels S, Lally C and MacDonald B 2013 Surface modification of absorbable magnesium stents by reactive ion etching Plasma Chem. Plasma Process. 33 1137–52

[32] Zhou K et al 2021 Nano-micrometer surface roughness gradients reveal topographical influences on differentiating responses of vascular cells on biodegradable magnesium Bioact. Mater. 6 262–72

[33] Li P, Zhou N, Qiu H, Matiz M F, Wang J and Huang N 2018 In vitro and in vivo cytocompatibility evaluation of biodegradable magnesium-based stents: a review Sci. China Mater. 61 301–15

[34] Hanas T, Sampath Kumar T S, Perumal G and Doble M 2016 Tailoring degradation of AZ31 alloy by surface pre-treatment and electrospun PCL fibrous coating Mater. Sci. Eng. C 65 43–50

[35] Ostrowski N et al 2013 Acta biomaterialia corrosion protection and improved cytocompatibility of biodegradable polymeric layer-by-layer coatings on AZ31 magnesium alloys q Acta Biomater. 9 8704–13