Computational Modeling of the Corrosion Process and Mechanical Performance of Biodegradable Stent

JiaYu Tao, Jie Cheng*, GuTian Zhao, Xue Hu, XingZhong Gu, JunJie Su
School of Mechanical Engineering, Southeast University, Nanjing, China

cjgrace@sina.com

Abstract. Magnesium alloy stents have drawn increasing research interest in recent years owing to their biodegradable behaviors. As dissolved by corrosion, mass of the magnesium alloy stents decreases with time, allowing mechanical load to gradually transfer to the surrounding tissues. This work aimed to develop a numerical model based on Continuum Damage Mechanics (CDM) combining pitting corrosion and stress corrosion crack to better predict the degradation behavior of biodegradable magnesium alloy stent. It was applied in coronary stents through finite element method compared with the use of single pitting corrosion model. The results indicated that addition of stress corrosion attack accelerated the degradation rate and support performance loss of stent compared with single pitting corrosion. The proposed model would bring new sights to simulation and serve the design of magnesium alloy stents.

1. Introduction
Biodegradable magnesium alloy stents (MAS) have attracted much attention in recent years as they can provide temporary mechanical support for the heart artery after angioplasty procedure to prevent elastic rebound[1,2]. The specific characteristic of MAS to be completely absorbed by matrix is beneficial for young patients[3,4], and has the potential to reduce some of the long term health risks such as in-stent restenosis and late stent thrombosis[5,6].

However, the main challenge of MAS design lies in that they degrade too fast, which can not guarantee sufficient mechanical support. Therefore, it is necessary to study the degradation mechanism and corrosion rate of MAS, especially the impact of the degradation process on the mechanical integrity. As described by D. Gastaldi[7], the mechanisms affecting the corrosion behavior of magnesium-based stents can be: micro-galvanic corrosion, localized corrosion, stress corrosion cracking (SCC) and fatigue corrosion.

Finite element analysis has been an important tool for modeling MAS degradation. Based on Continuous Damage Mechanics (CDM), several numerical models have been proposed. Uniform corrosion is an approximate representation of micro-galvanic corrosion if alloy elements’ distribution in material is homogeneous and it is may be the simplest form of degradation modeling as the assumption is highly idealized and relatively unrealistic. In reality, micro-galvanic corrosion is usually observed as heavy localized and more common in chlorine-containing solution, therefore pitting corrosion is more suitable to describe these two mechanisms[7]. J A etc.[8] compared uniform corrosion and pitting corrosion results and found that pitting corrosion can greatly reduce the mechanical strength of samples, which is closer to the experimental results, while the results of
uniform corrosion simulation are quite different. After undergoing crimping and expanding, the residual stress and blood environment can lead to SCC, which is dangerous as it can lead to fast fracture[9]. Wu et al.[10] linearly superimposed the uniform corrosion and SCC models to optimize the stent design. During the stent service period, the fatigue corrosion is caused by the interaction of pulsatile stress and the aggressive blood environment[9]. A handful of people have studied fatigue corrosion while the results showed that fatigue corrosion didn’t dominate the total mass loss and accounted for a small proportion[11].

Up to now, some research focuses on single degradation form such as uniform or pitting corrosion without considering the importance of SCC. Some others developed enhanced model such as coupled formulation of uniform corrosion and SCC, while neglecting the fact that magnesium stents do not corrode uniformly but rather focally as shown in qualitative micro CT assessment[12]. However, there are relatively rare studies on the corrosion model combining pitting corrosion and SCC. In order to better predict the effect of degradation on mechanical properties of magnesium alloy stents, in this paper, a phenomenological model combining pitting corrosion and SCC was established, implemented in commercial finite element software through user subroutines.

2. Methodology

2.1. Geometry models and material properties
The geometry models are created via computer-aided design, with detailed dimensions shown in Figure 1. The stent material is adopted from an extruded magnesium alloy of AZ31, consisting of Al 0.03, Zn 0.01, Mn 0.002 and Mg balance (mass percentage), and the true stress-strain curve is shown in Figure 2[8]. It has a modules of 43.5GPa, Poisson’s ratio of 0.35 and density of 1.77 g/cm³, which was modeled as a homogeneus, isotropic, elastoplastic material. A tri-folded balloon geometry is constructed and secured to the delivery system with the material property based on the model by Chen[13] et al. It is modeled as an isotropic, elastic material with the Young’s modulus and Poisson’s ratio to be 900Mpa and 0.3, respectively.

2.2. Degradation model
Based on Continuum Damage Mechanics theory, a degradation model combining pitting corrosion and stress corrosion crack was established. The theory allows considering the effect of corrosion on reduction on microscopic structural integrity by introducing scalar damage parameter and effective stress tensor $\sigma_i$ [14]:

$$\tilde{\sigma}_i = \sigma_i (1 - D)$$

(1)

where $\sigma_i$ is the Cauchy stress tensor. In the damage model, the material damage is considered element-by-element, and the corrosion damage variable $D$ is monotonically increasing from undamaged ($D = 0$) to totally damaged ($D = 1$).
The corrosion damage variable \( D \) is considered as a linear superposition of pitting and SCC:

\[ D = D_p + D_{sc} \]  

(2)

The pitting corrosion damage \( D_p \) is defined to describe the corrosion when the material is exposed to the aggressive environment and the damage evolution law is as the following equation:

\[ \frac{dD_p}{dt} = \frac{\delta_u K_u \lambda_p}{L_e} \]  

(3)

where \( \delta_u \) is the material characteristic length, \( L_e \) is the model characteristic length and \( K_u \) is the corrosion kinematic parameter, as described in [7]. \( \lambda_p \) is a randomly distributed element-specific pitting parameter generated on the standard Weibull distribution[15]. The characteristic length of the material is 0.017 mm, consistent with the grain size of the AZ31 alloy observed in[16].

The \( D_{sc} \) represents the damage caused by SCC. The evolution law of SCC processes can be expressed by the following equations:

\[ \frac{dD_{sc}}{dt} = 0, \sigma_{eq}^* < \sigma_{th} \]  

(4)

\[ \frac{dD_{sc}}{dt} = \frac{L_e}{\delta_{sc}} \left( \frac{S \sigma_{eq}^*}{1 - D} \right)^s, \sigma_{eq}^* \geq \sigma_{th} \geq 0 \]  

(5)

\( \sigma_{eq}^* \) is the equivalent stress to control the stress corrosion process. \( \sigma_{th} \) is the threshold stress above which stress corrosion occurs, ranging from 30% of the yield stress to 90% of the ultimate tensile stress[17]. In this paper, \( \sigma_{th} \) is set as 50% of the yield stress. \( \delta_{sc} \) is the stress corrosion characteristic dimension. \( S \) and \( R \) are dynamic constants related to the stress corrosion process. When the \( pH \) value of the corrosion environment is stable, \( S \) and \( R \) are suggested to adopt a constant value[18]. The details of pitting corrosion and SCC relevant parameters are listed in table 1, sourced from the values of the same material magnesium alloy AZ31[19].

**Table 1. Parameters for material degradation model.**

| Parameter | Value |
|-----------|-------|
| \( L_e (mm) \) | \( \delta_u (mm) \) | \( \delta_{sc} (mm) \) | \( K_u (h^{-1}) \) | \( \sigma_{eq} (MPa) \) | \( S (mm^2 h^{-0.5} N^{-1}) \) | \( R \) |
| \( \approx 0.04 \) | 0.1 | 0.067 | 0.0065 | 80 | 0.003 | 2 |

2.3. FEA model and loading steps

In FEA model, the catheter shaft and 12 crimping plates were meshed with discrete rigid elements (R3D4). The folded balloon and stent were meshed with reduced integration linear membrane elements (M3D4R) and brick elements (C3D8R), respectively. General contact algorithm was used in Abaqus/Explicit to allow automatic redefinition of contact surfaces following element removal by Abaqus solver[20]. For normal contact, the default “hard” contact was set and for tangential contact, the friction coefficient was assumed to be 0.2.

Two models were established and Model 2 considered the combination of pitting corrosion and SCC while Model 1 used as the control group only considered the pitting corrosion.

There were five simulation steps executed for the whole simulation. The first four simulations were stent implantation procedures where no corrosion was considered. Initially, a radial displacement was applied through 12 rigid plates to reduce the outer stent diameters to 1.5 mm (step1). Next, the crimping plates were removed to allow the stent to recoil (step 2). After that, the balloon was inflated with the inner surface pressure of 3 Mpa to give a maximal stent outer diameter to be 3.75 mm (step 3).
And then the stent recoiled again with the release of pressure (step 4). The whole model and its results after step 4 were imported in the following step where the corrosion environment was taken into account. It was achieved through the Abaqus user subroutine VUSDFLD and the simplified flowchart outlining the corrosion process is shown in Figure 3. Without an experimental-based identification degradation parameters, degradation step time doesn’t have the absolute physical meaning, but represents an evolutionary variable for comparison. In this paper, the time that the stent is implanted into corrosion environment is set as the start time of 0 and the time for stent’s occurrence of breakage is set as $t^*$. 

**Figure 3.** Simplified flowchart of degradation model.

**Figure 4.** Von Mises stress distribution after stent implantation: (a) crimping (b) recoil (c) expansion (d) recoil again.

### 3. Results and discussion

Mass loss ratio was calculated as an evaluation criterion to compare two models. The formulation of mass loss ratio can be expressed as follows:

$$mass \ loss \ ratio = \frac{M_{initial} - M_i}{M_{initial}}$$

(6)

where $M_{initial}$ indicates the mass when the stent is not degraded and $M_i$ means the stent mass at degradation step time $t$.

As the material density of the stent is assumed to remain constant during degradation and based on the theory that $M = \rho V$, the simplified form can be obtained:

$$mass \ loss \ ratio = \frac{V_{initial} - V_i}{V_{initial}}$$

(7)

where $V_{initial}$ is the total element volume before degradation and $V_i$ is the existing element volume.

Figure 4 illustrates the von Mises stress distribution of stent after the first four loading steps. It can be seen that after the implantation procedure, high stress is still concentrated at the crown of stent where the maximum value reaches up to 315.50 MPa and the value is obviously above the giving threshold stress ($\sigma_{th}$) of 80 Mpa.
Figure 5. Comparison of mass loss ratio of stent.

Figure 6. von mises stress and damage distribution at 0.1 t*: (a) von mises stress (b) total damage (c) pitting damage (d) stress corrosion crack damage (I) partial enlargement (II) partial enlargement at 0.1 t* (III) partial enlargement at 0.75 t*.

Figure 5 displays the mass loss ratio curves of two degradation models. Both curves show linear growth in early degradation stage (before 0.2 t*), and then the slope of two curves decreased gradually, indicates the reduction of degradation rate. The phenomenon coincides with the trend of stent mass loss in vitro degradation experiment as described in[21]. It can be found that the mass loss ratio curve of Model 2 is always above that of Model 1, and the difference between them increases over the degradation time, from the initial difference of 0.2% to the final difference of 11%.

Combined with the von mises stress distribution contour and corrosion damage value contour shown in Figure 6, we can learn that pitting corrosion is randomly distributed (Figure 6(I)) while SCC is concentrated at the crown of the stent most on inner surfaces (the left partial enlargement of Figure 6(d)) where higher residual stress exists (with the maximum value to be 315.75 MPa) after the crimping-expanding process. The accumulated damage at the crown aggravates the degradation degree and mass loss. The location of stent’s crown is also the place where fracture occurs first (Figure 6(III)). Besides, at 0.1 t*, the pitting corrosion damage maximum value comes up to 1. The stress corrosion damage value for most elements on stent is below 0.17 and the maximum value is 0.26, indicating that pitting corrosion is still dominant for the total damage.

Figure 7. Total corrosion damage over time: (a) 0.25 t* (b) 0.5 t* (c) 0.75 t*

Figure 8. Radial strength over stent outer diameter during re-crimping process at
(d) 1 $t^*$. different degradation time.

Figure 7 illustrates the change of total damage value over degradation time. At 0.25 $t^*$, damage value of a few elements come up to 1 and most elements’ damage value is below 0.67. And at 0.5 $t^*$, the total damage value of elements at the crown increases obviously, with value above 0.75. When the degradation time reaches 0.75 $t^*$, the stent crown becomes thinner due to more mass loss and shows evident facture occurrence at 1 $t^*$. The loss of stent elements in simulation is an expression of material spalling and even fracture in degradation experiment.

The radial strength is another evaluation index to represent the support performance of stent structure. It is characterized by the reaction force related to a sudden reduction in the stent diameter, or if there is no obvious point of collapse, it is derived from the reaction force when the diameter loss equals 10% [19]. It can be achieved by imposing radial compression to stent again with rigid plates. According to ASTM F3067 [22], the radial strength can be calculated as:

$$R = \frac{F_R}{A}$$

(8)

$$A = \pi DL$$

(9)

where $F_R$ indicates the radial force, $D$ is the instant outer diameter of stent and $L$ is the initial length of stent.

Figure 8 displays the radial strength of the stent at the same simulation time with two degradation models. The stent outer diameter was reduced from 3.63 mm to 3.24 mm through re-crimping procedure and the radial strength according to the diameter of 3.24 mm was taken for comparison. The intact device can withstand a maximal load of 0.986 MPa, corresponding very well to the value around 15 N reported in [23]. Due to the slight cumulative damage caused by SCC, the two radial strength curves almost coincide at the degradation time of 0.1 $t^*$, which is also consistent with a difference of 0.9% mass loss ratio between the two models. Nevertheless, with the increase of degradation time, the radial strength of Model 2 decreases significantly, compared with that of Model 1. The radial strength reduction of Model2 is 72.1% at 0.5 $t^*$, which is lower than that of Model 1 to be 49.8% at the same degradation time. Therefore, quantitative comparison indicates that with the increase of time, the cumulative amount of SCC damage increases and SCC accelerates the loss of mechanical performance of stent.

4. Conclusion

In this work, a computational corrosion model combing pitting corrosion and stress corrosion crack was developed and utilized in biodegradable magnesium alloy stent evaluation. The mass loss ratio and radial strength of stent were assessed from simulation results. The mass loss curve obtained in simulation in this paper is consistent with that observed in vitro degradation experiment in [21]. The analysis revealed that stress corrosion crack has an important effect on the acceleration of mass loss ratio and loss of radial support. In the future work, by changing degradation parameters in this model, the simulation results can be matched with experimental results. Moreover, the study can be further developed to study the influence of fatigue corrosion on stent structure through applying cyclic loading conditions. The numerical framework presented in this study could be used to predict the degradation process and dangerous section of structure to provide a convenient design and testing tool for biodegradable alloy stents.

5. References

[1] Serruys P W, De Jaegere P, Kiemeneij F, Macaya C, Rutsch W, Heyndrickx G, Emanuelsson H, Marco J, Legrand V and Materne P et al 2016 Benestent Study Group. J. N Engl J Med. 331(8) 489-495.
[2] Zheng Y F, Gu X N and Witte F 2014 Biodegradable metals. J. Material science & Engineering. R 77 (mar.) 1-34.

[3] Erbel R, Bose D, Haude M, Kordish I, Churkidze S, Malyar N, Konorza T and Sack S 2007 Herz 32 308–319.

[4] Schranz D, Zartner P, Michel-Behnke I and Akiunr W 2006 Catheter. Cardiovasc. Interv. 67 671–673.

[5] Mitra AK and Agrawal DK 2006 J. Clin. Pathol 59 232e9.

[6] Daemen J, Menaweser P, Tschida K, Abrecht L, Vaina S, Morger C, Kukreja N, Jiini P, Sianos G and Hellige G et al 2007 Digest of the World Core Medical Journals 369 (9562) 667e78.

[7] Gastald D, Sassi V, Petrini L, Vedani M, Trasatti S and Migliavacca F 2011 Journal of the Mechanical Behavior of Biomedical Materials 4(3) 352-365.

[8] Grogan J A, O’Brien B J, Leen S B and McHugh P E 2011 Acta biomaterialia 7(9) 3523-3533.

[9] Cui X, Peng K, Liu S, Ren Q and Qiao A 2019 Procedia Structural Integrity 15 67-74.

[10] Wu W, Gastaldi D, Yang K, Tan L, Petrini L and Migliavacca F 2011 Materials Science & Engineering B 176 1733-1740.

[11] Shen Z, Zhao M, Zhou X, Yang H, Liu J, Guo H, Zheng Y, Yang JA 2019 Acta biomaterialia 97 671-680.

[12] Deng C Z, Radhakrishnan R, Larsen S R, Boismer D A, Stinson J S, Hotchkiss A K, Petersen E M, Weber J and Scheuermann T 2011 Magnesium Technology (John Wiley & Sons, Ltd/ Springer International Publishing) pp413-418.

[13] Chen C X, Chen J H, Wu W, Shi Y J, Jin L, Petrini L, Shen L, Yuan G Y, Ding W J, Ge J B, Edelman E R and Migliavacca F 2019 Biomaterials 221.

[14] Lemaître J and Desmorat R 2005 Engineering damage mechanics: ductile, creep, fatigue and brittle failures (Berlin Heidelberg: Springer-Verlag) chapter 5 pp 233-276.

[15] Grogan J A, Leen S B and McHugh P E 2013 Biomaterials 34(33) 8049–8060.

[16] Del Valle JA, Perez-Prado MT and Ruano OA 2005 Metall Mater Trans A. 6 1428–38.

[17] Winzer N, Atrens A, Song G L, Ghali E, Dietzel W, Kainer K U, Hort N and Blawert C 2005 Adv. Eng. Mater. 7 659–693.

[18] da Costa-Mattos H S, Bastos I N, Gomes J A C P 2008 Corros. Sci. 50 2858–2866.

[19] Arnout Oppeel 2014-2015 Experimental characterization and finite element modeling of biodegradable magnesium stents (Belgium: Gent University).

[20] Anon. Abaqus Theory Manual (Version 6.10). Providence, RI: DS SIMULIA; 2010.

[21] Wu W, Chen S, Gastaldi D, Petrini L, Mantovani D, Yang K, Tan L L and Migliavacca F 2013 Acta Biomaterialia 9(10) 8730-8739.

[22] 2017 Standard Test Method for Measuring Intrinsic Elastic Recoil of Balloon Expandable Stents (US: ASTM F2079).

[23] Shimizu Ichiro, Wada Akira and Sasaki Makoto 2018 A Study on Designing Balloon Expandable Magnesium Alloy Stent for Optimization of Mechanical Characteristics (MDPI vol 2(8)) (Belgium: Brussels) p 523.

Acknowledgments
The research was supported by the National Natural Science Foundation of China (51775107, 51575106), and the Industry-University-Research Prospective Joint Research Project of Jiangsu Province (BY2015070-12).