**A study of long-term static load on degradation and mechanical integrity of
Mg alloys-based biodegradable metals**

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Abstract: Predicting degradation behavior of biodegradable metals *in vivo* is crucial for the clinical success of medical devices. This paper reports on the effect of long-term static stress on degradation of magnesium alloys and further changes in mechanical integrity. AZ31B (H24) and ZE41A (T5) alloys were tested to evaluate stress corrosion cracking (SCC) in a physiological solution for 30 days and 90 days (ASTM G39 testing standard). Scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX) and micro-computed tomography (micro-CT) were used to characterize surface morphology and micro-structure of degraded alloys. The results show the different mechanisms of stress corrosion cracking for AZ31B (transgranular stress corrosion cracking, TGSCC) and ZE41A (intergranular stress corrosion cracking, IGSCC). AZ31B was more susceptible to stress corrosion cracking under a long term static load than ZE41A. In conclusion, we observed that long-term static loading accelerated crack propagation, leading to the loss of mechanical integrity.

Keywords: stress corrosion cracking, biodegradable metals, four-point bending, magnesium

Introduction

Biodegradable metals are expected to degrade gradually *in vivo*, with an appropriate host response while it provides mechanical strength at the initial stage of implantation and slowly be absorbed to the human body. Three metal alloys including magnesium based alloys [1-3], iron based alloys [4, 5] and zinc based alloys [6, 7] are recently explored as biodegradable metals which can dissolve completely upon fulfilling the mission to assist with tissue healing without leaving any trace. However, complex physiological stresses make biodegradable metals degradation unpredictable, which is one of the challenges for industrial success. Implantable devices in general are subjected to acute dynamic loadings during normal physical activities [8], which can cause stress corrosion cracking (SCC) [9-15] and corrosion fatigue (CF) [13, 16, 17]. A majority of permanent implant failures are caused by SCC and CF [18-20] after exposure to physiologically stressed environments. However, in case of magnesium alloy based biodegradable metals, higher stress over intrinsic maximum stresses of alloys or threshold stress of SCC can be built by degradation process, which can cause earlier failure of medical device [9-14, 17]. A key step is to identify well-defined fracture mechanisms of magnesium alloys under the stress conditions that can be caused from various physiological environment using simplified and standardized *in vitro* test method that can get similar results from *in vivo* until tissues are recovered with enough strength (8-12 weeks). Clear understanding of the relationship between corrosion and mechanical stress can help to design better alloy and medical devices to resist to cracking/fracture.

The magnesium-based biomaterials are under complicated stress conditions like tensile, compressive, bending, shear stresses and distortion during the physical activity after surgery. Implanted surgical pins, screws, and plates can be put under static and dynamic stresses by fixation on irregular bone shape and body weight, and can be three to five times more increased by dynamic stresses during ordinary activities like walking and running [21]. The question is how these complex stresses affect magnesium degradation in terms of degradation rate, uniform degradation, mechanical integrity, localized degradation, product formation, and time-lapse degradation. It is necessary to evaluate the SCC susceptibility of magnesium alloys in simulated physiological conditions with the appropriate testing method. SCC can be caused by

concentration of stress at a localized corrosion area, cyclic load and hydrogen embrittlement (HE) during the *in vivo* degradation process [22], which can possibly induce sudden fracture under theoretically expected fracture stress limit in shorter life time. Most of SCC studies were done using a slow strain-rate technique over a short term period [10,14, 23-25], long-term study with better *in vivo* mimicking environment is critical to understand effect of stress on mechanical and degradation integrity.

This paper investigates the effect of long-term loading on degradation magnesium alloys in terms of corrosion rate, product formation, pitting, crack propagation, and mechanical integrity. The SCC test is conducted with ASTM G39 standard (four-point static load) in Hank's Balanced Salt solution with representative magnesium alloys, AZ31B (H24) and ZE41A (T5). We explore mechanism of SCC through well characterization of surface morphology and micro-structure.

2. Materials and methods

2.1. Materials and stress corrosion cracking test

Certified magnesium alloy coupons, AZ31B (2.5-3.5% Al, 0.7-1.3% Zn, 0.2 % Mn, H24) and ZE41A (3.5-5.0 % Zn, 0.1-1.7% RE, 0.4-1.9% Zr, T5) were purchased from Metal Samples (division of Alabama Specialty products Inc., Munford, AL). SCC test was conducted with two magnesium alloys (AZ31B (H24), and ZE41A (T5)) in Hank's Balanced Salt solution and it was followed by ASTM G39 testing standard (four-point bending load). In terms of number of samples for SCC test, we studied 13 samples of AZ31B (3 blank samples for control, 3 samples for 30-day immersion, 3 samples for 30-day immersion with stress, 2 samples for 90-day immersion and 2 samples for 90-day immersion with stress). We tested the same number of ZE41A SCC test. We also examined 3 samples for each alloy for tensile tests. The samples were mechanically polished to remove the oxide layer sequentially with 800, 1000, and 1200 grit silicon carbide paper with isopropyl alcohol. Specimens were then ultrasonically cleaned sequentially with acetone and ethanol, and dried using nitrogen stream.

ASTM G39 loading frame and 316L ASTM G39 four-point bent beam loading clamp were purchased from Metal Samples (Fig. 1) which can simulate stresses of tensile and compression on specimens. We

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4 applied static load, 120 MPa between the inner supports and the required deflection was calculated from
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6 the formula given in ASTM G39. In brief, applied displacement under 120 MPa between the inner
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$$\sigma = 12 \cdot E \cdot t \cdot y / (3L^2 - 4a^2) \quad (1)$$

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17 where, σ is applied tensile stress, E is the elastic modulus, t is the specimen thickness, y is the
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19 maximum deflection, L is the distance between outer supports and a is the distance between outer and
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21 inner supports. We neglected creep effect.
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24 The accuracy of this experimental method was verified by measuring deflection on one sample using a
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26 strain gauge. We screwed the main loading frame to bend specimens and deflection was also measured
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28 using a dial gauge (accuracy of approximately $\pm 0.01\text{mm}$). The four deflected specimens were immersed
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30 in Hank's Balanced Salt solution [3] (solution volume per specimen was 2L) for 30 days and 90 days.
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32 Standard immersion test for AZ31B and ZE41A as controls was also performed. All the system was
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34 incubated in an incubator (37 °C) in Hank's Balanced Salt solution (ASTM G39 standard). And pH was
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36 measured every 5 days followed by fresh solution change. The change of mechanical properties after SCC
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38 for 30 and 90 days test were measured and compared with the mechanical properties of alloys after
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40 standard immersion test to identify the effects of bending stress.
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Figure 1. Four-point bending test apparatus and specimen for stress corrosion cracking test in Hank's Balanced Salt solution. (a) ASTM G39 test apparatus and ZE41A specimen, and (b) Stressing holder with a deflection gage. $a = 22.25$ mm, $L = 89$ mm, $l = 44.5$ mm.

Table 1. Experimental summary for stress corrosion cracking test.

Classification	Description
Alloys	AZ31B (H24) and ZE41A (T5)
Maximum deflection (y)	AZ31B (3.11 ± 0.03 mm), ZE41A (2.80 ± 0.04 mm)
Solution and volume ratio	Hank's Balanced Salt Solution, 45ml/cm^2
Test duration	30 and 90 days
Evaluation	Weight loss, SEM, CT, Mechanical properties (E, YS)

2.2. Microstructure observation

The alloy grain structure was observed under a field emission scanning electron microscope (SEM, SU8000, Hitachi, Japan) after etching with 10% Nital solution and then cleaning with isopropanol

solution. Grain sizes were measured using Image-Pro plus 6 software (Media Cybernetics, Inc. MD, USA).

2.3. Mechanical test

Mechanical property of the magnesium alloys for four-point bending test (flexural stress-flexural strain curves) was acquired by using Instron (5542, USA) under force control with the same configuration (Fig. 1). Stainless steel pins replaced by the screw in Fig. 1 was used to apply load with a load cell ($\pm 500\text{N}$, Instron) and an extensometer (extensometer GL2in, Instron, USA) was used to measure displacement. The beam was subjected to four-point flexural loading at constant rate with initial strain-rate of 0.5 mm/min until the occurrence of maximum stress/maximum load at room temperature. The four-point loading tests were performed right before slip of specimen by loading. Flexural stress and strain were calculated from the following equations [26, 27],

$$\delta = \frac{S(\%) - S_0(\%)}{k} \quad (2)$$

$$E = \frac{Pa(3L^2 - 4a^2)}{4bh^3\delta} = \frac{P}{\delta} \frac{a(3L^2 - 4a^2)}{4bh^3} \quad (3)$$

$$\sigma = \frac{3Pa}{bh^2} \quad (4)$$

$$\varepsilon = \frac{48h\delta}{11L^2} \quad (5)$$

where, E is elastic modulus, L is span length (m) between supports, b is specimen width (m), h is specimen thickness (m), P is load increment as measured from preload, δ is deflection increment at midspan as measured from preload, a is the distance (m) from the support to the load applicator when the specimen is straight. S is measured strain, S_0 is initial strain, and k is calibrated stain gauge slope. The yield strength was calculated from plot flexural stress-strain and 0.05% offset. Standard tensile test was also performed with the same AZ31B and ZE41A (tensile sample dimensions, 50 ± 0.5 overall length, 15

length of grip section, 15.528 ± 0.1 length of reduced parallel section, 5 ± 0.1 width of grip section, 5 ± 0.1 width, 3 ± 0.05 thickness, unit: mm) purchased from Metal Samples. Load-displacement data was acquired by tensile test using Instron 5542. The yield strength was calculated by 0.2% offset from stress-strain curve.

2.4. Samples characterization

The samples were captured using digital photography before and after four-point stressed immersion test. 3D images and cross-sectional images of the samples were acquired using micro-computed tomography (micro-CT, Phoenix Nanotom-MTM, GE Sensing & Inspection Technologies GmbH, Germany). X-ray emission parameters of micro-CT were 80 kV and 180 μ A. Analysis of the reconstructed volumes generated by CT was conducted using methods published previously [28]. Surface analysis of AZ31B and ZE41A alloys were acquired using a scanning electron microscope (SU8000, Hitachi, Japan) after gold/palladium sputter coating. The samples for cross-sectional investigation of crack propagation were prepared by polishing after mounting with epoxy resin (Epokwick® epoxy resin, Buehler, USA).

3. Results and Discussion

As the control experiment, we measured flexural stress-strain AZ31B and ZE41A from four-point bending and stress-strain curve from standard tensile test. Fig. 2a shows flexural stress-strain from four-point bending test of AZ31B and ZE41A and inset shows apparatus for four-point bending test. The mechanical properties calculated from the four-point bending experiment were compared with the results from stress-strain curves after 30 and 90 days immersion with/without stress. Fig. 2b shows the stress-strain curves of AZ31B and ZE41A from the tensile test (inset shows specimens) which includes modules, yield strength, and ultimate strength (Table 2) [28-31].

Figure 2. (a) Flexural stress-strain from four-point bending test of AZ31B and ZE41A (inset shows four-point bending test), and (b) Tensile stress-strain curves from tensile test (inset shows tensile specimens).

Table 2. Summary of tensile and flexural mechanical test with AZ31B and ZE41A ($n=3$).

Alloy	Tensile		
	Elastic modulus (GPa)	Yield strength (MPa, 0.2% offset)	Ultimate tensile stress (MPa)
AZ31B	43 ± 0.3	211 ± 1.7	286 ± 3.6
ZE41A	42 ± 1.3	148 ± 1.9	249 ± 2.5
	Flexural		
	Flexural modulus (GPa)	Yield strength (MPa, 0.05% offset)	Ultimate flexural stress (MPa)
AZ31B	45 ± 0.1	214 ± 17.3	286 ± 7.7
ZE41A	45 ± 0.3	154 ± 4.9	251 ± 9.5

Figure 3. Microstructures of AZ31B (left) and ZE41A surface (right).

We characterized the microstructure of AZ31B and ZE41A in terms of grain size/structure, secondary phases and impurity. Fig. 3 shows that AZ31B has grain sizes from $2.4 \pm 0.4 \mu\text{m}$ with secondary phases as bright dots. Even though data was not shown, we did not observe different microstructure morphology between longitudinal and transverse directions. ZE41A shows an equiaxed grain structure of α -Mg matrix, with a grain size about $70.8 \pm 18.9 \mu\text{m}$. A second phase is clearly visible at the grain boundaries which contains a main quantity of zinc and rare earths (RE: lanthanum and cerium) identified as $\text{Mg}_7\text{Zn}_3\text{RE}$ [32]. Zirconium is dissolved in the α -Mg matrix. Mg alloys can be classified by two classes; i) Zr containing alloys and ii) Zr-free alloys. Zr-containing ZE41A reacts with impurity elements removing them from the melt so that ZE41A has typically high purity with low corrosion rates. **On the other hand, corrosion resistance of AZ31, Zr-free alloy is highly dependent on the impurity content.**

Fig. 4a-b shows optical images of AZ31B and ZE41A after immersion for 90 days with/without static load. Optical images show that ZE41A has higher corrosion rate than AZ31B. ZE41A also has more product formation on the surface than the surface of AZ31B. Fig. 4c shows summary of weight loss for AZ31B and ZE41A samples after immersion tests with/without stress for 90 days. We observed that AZ31B shows more difference between without and with stressed condition than ZE41A. ZE41A

degraded much faster than AZ31B, which might be the reason for white product formation on ZE41A surface (Fig. 4b). ZE41B also gradually degraded over 90 days but AZ31B degraded fast at the initial stage and leveled off for both with/without stressed samples [9, 33]. There was a report that the ultimate tensile strength (UTS), yield strength (YS) and elongation (EL) of the Mg-2Zn-0.8Zr samples with immersion decreased rapidly at first and then decreased slowly [11].

Figure 4. Surface morphology and corrosion analysis of AZ31B and ZE41A after immersion for 90 days with/without stress. (a) Representative AZ31B optical images, (b) Representative ZE41A optical images, (c) Summary plot of weight loss measurement ($n=2$).

Fig. 5a shows SEM images (surface and cross-section) after immersion of stressed AZ31B for 30 days and 90 days. After removal of the corrosion product, we observed that AZ31B has localized pitting corrosion partially covered on the surface. Cracks were interestingly propagated on the localized pitting sites, which created deep a dimple during long-term immersion test. On the other hand, we did not observe any cracks for the AZ31B sample which does undergo stress. We further etched a cross-section of the stressed AZ31B to explore SCC mechanism. As shown in Fig 6a, low and high resolution of etched

cross-section images show crack propagation is clearly transgranular stress corrosion cracking (TGSCC). Fig. 5b shows SEM images (surface and cross-section) after immersion of stressed ZE41A for 30 days and 90 days. Corrosion was more uniformly occurred along with grain boundary, which has secondary phase with zinc and rare earths. We further etched cross section of stressed ZE41A samples to explore SCC mechanism. As shown in Fig 6b, low and high resolution of etched cross-section images show that crack is clearly propagated along with grain boundary which shows typical intragranular stress corrosion cracking (IGSCC). Similar results report that rare-earth containing magnesium alloys such as ZE41, QE22 and EV31A had higher susceptibility to IGSCC in 0.5 wt.% NaCl solution which was associated with second-phase particles along grain boundary [14]. Fine-grained AZ80 exhibited TGSCC.

Figure 5. Surface and microstructure analysis. (a) SEM images (surface and cross-section) after immersion of AZ31B under stress for 30 days (top) and 90 days (bottom), (b) SEM images after immersion of ZE41A under stress for 30 days (top) and 90 days (bottom).

Figure 6. Etched cross-section images of AZ31B and ZE41A after 90-day immersion under stress. (a) and (b) Low and high resolution of crack propagation in AZ31B, (c) and (d) Low and high resolution of crack propagation in ZE41A.

Figure 7. Micro-CT based surface morphology and microstructure analysis. (a) AZ31B with transgranular stress corrosion cracking (TGSCC), (b) Enlarged surface analysis (7mm × 7mm) of AZ31B, (c) Enlarged cross-sectional analysis for localized corrosion under stress of AZ31B, (d) ZE41A with intergranular stress corrosion cracking (IGSCC), (e) Enlarged surface analysis (7mm × 7mm) of ZE41A, (f) Enlarged cross-sectional analysis for localized corrosion under stress of ZE41A.

Fig. 7 shows micro-CT images of AZ31B and ZE41A with and without stress for 30 days and 90 days. These results also confirmed that AZ31B crack was propagated with transgranular stress corrosion cracking (TGSCC) and ZE41A crack was propagated with intergranular stress corrosion cracking (IGSCC) [14]. Crack size for AZ31B was about 50 μm size for 30 days immersion sample with stress (Fig. 5a). As shown in Fig. 6d-f, micro-CT images for ZE41A show product, in which crack propagation occurred, along the grain boundaries (confirmed IGSCC). More localized degradation was found on the center region (maximum stressed surface).

Fig. 8a shows micro-CT images with depth (50 μm to 400 μm) from the surface of AZ31B and ZE41A after the 90 day test. The amount of pitting (black area) was increased for stressed AZ31B and ZE41A. Fig. 8b shows summary of degradation area from surface to 500 μm depth. Stressed ZE41A has large degradation area with depth, which shows more localized corrosion and stress corrosion cracking. We observed the same behavior for stressed AZ31B (inset of Fig. 8b).

Figure 8. Micro-CT analysis of pitting with depth. (a) Micro-CT images with depth from tensile stressed surface of AZ31B and ZE41A after 90 days test, (b) Plots of AZ31B and ZE41A surface degradation from surface to 500 μm depth. Each sample size: 7 mm $\times$ 7 mm.

Fig. 9 shows mechanical properties from four-point bending tests before and after 90 days immersion with/without stress. We observed overall decrease of flexural stress (Fig. 9a), elastic modulus (Fig. 9b), yield strength (Fig. 9c), and maximum strength (Fig. 9d) for both stressed AZ31B and ZE41A [10]. Even though we did not show 30 days immersion test results, it was not statically significant. Long-term static loading can affect degradation and mechanical integrity of Mg alloys under a stressed environment. Long-term static loading is a critical factor to understand how complex mechanical loadings in the human body can affect mechanical degradation of devices, which need to reflect as an important parameters to design better alloys such as (new alloying element, process, heat treatment for grain refinement and rapid solidification).

Figure 9. Mechanical properties from four-point bending tests before (blank) and after immersion with/without stress for 90 days: (a) Representative flexural stress-strain curves, (b) Elastic modulus, (c) Yield strength, and (d) Maximum strength of AZ31B and ZE41A. Blank: n = 3, corroded alloys: n = 2.

SCC occurs in two different ways, IGSCC and TGSCC. Different mechanisms describing TGSCC and IGSCC processes have been also suggested from previous literatures. However, all these mechanisms show relatively good agreement for some special cases, but in general it is still not well understood because of complex interaction between alloying elements, applied stress, and environment. In this long-term SCC study, microstructure analysis (Fig. 3) shows that AZ31B has fine-grained size. SCC test results show that AZ31B was corroded at some localized areas which have a brittle appearance corresponding to propagate crack possibly associated with beta-phase particles (Fig.10a) [32]. This crack propagation can further enhance localized corrosion, leading to the decrease of mechanical integrity. No evidence of corrosion associated with the grain boundaries was found in this experiment. Similar results were also reported by Stampella et al [37] agreeing that crack morphology was determined by the grain size and that for fine-grained Mg alloy, SCC was exclusively transgranular whereas for larger grained Mg SCC was mixed transgranular and intergranular. TGSCC in stressed AZ31B is most likely caused by an embrittlement mechanism with discontinuous and fine-grain size. On the other hand, Microstructure of ZE41A shows coarse-grain size ($> 70 \mu\text{m}$) with β -Mg-Zn-RE grain boundary phase, which grain boundary precipitates were observed in some part of the microstructure. The precipitates can possibly accelerate the electrochemical corrosion along the grain boundaries which is the main reason for IGSCC (Fig. 10b). Pardue et al [38] also suggested that IGSCC is a continuous and electrochemical process [14]. Long-term study shows that corrosion was mainly initiated along with grain boundary which contained larger amounts of zinc and rare earths (RE: lanthanum and cerium). Static load clearly accelerated this process which leads to loss of mechanical property.

Figure 10. Representative SEM images of crack propagation from 90 day stressed AZ31B and ZE41A in Hank's Balanced Salt solution. Corrosion product was removed to observe microstructure (arrows are the sites for crack).

Fig. 11 shows simplified representation for mechanical integration (a biodegradable device and tissue regeneration) with time (weeks) in a physiologically relevant load-bearing environment with the consideration of idealized uniform corrosion, localized corrosion and stress corrosion cracking. Ideally, a biodegradable device should slowly degrade to provide sufficient mechanical support as a regenerated tissue start to provide strength. This important balance strongly depends on the mechanical integrity and degradation properties of biodegradable devices. However, due to complex physiologically relevant load-bearing environment in the body, biodegradable devices can lose mechanical strength early via localized corrosion such as pitting, stress corrosion cracking and corrosion fatigue. It is critical to understand mechanical factors and their effects on mechanical degradation and feedback the knowledge to design better alloys and medical devices more resistant to cracking/fracture during degradation. Another important parameter for a biodegradable device is biocompatibility; the stent itself and its degradation products should cause no toxicity or inflammation to the surrounding sites. Biodegradable device go through the typical healing processes including inflammation (1st week), granulation (first two weeks) and remodeling (first four to 12 months) before its complete degradation. Localized corrosion and stress

corrosion cracking also can interfere and delay healing processes locally. It is critical to understand whether products form and particulates generate under stress-loading environment for clinical success of a medical device.

Figure 11. Simplified representation of mechanical integration (biodegradable device and tissue regeneration) with time (weeks) for load-bearing physiological with the impact of idealized uniform corrosion, localized corrosion and stress corrosion cracking.

Conclusions

Biodegradable medical device undergoes complex mechanical loadings, affecting degradation rate, local pitting, mechanical integrity, and biocompatibility. Through stress corrosion cracking (SCC) test followed by ASTM G39 standard, we found

- 1) stress corrosion cracks were occurred for both, but with different mechanism, TGSCC for AZ31B and IGSCC for ZE41A, and
- 2) long-term static loading accelerated crack propagation, leading to the loss of mechanical strength.

Acknowledgements

This work was supported by National Science Foundation (NSF) Engineering Research Center (ERC) for Revolutionizing Metallic Biomaterials (NSF-0812348) and NIH NIGMS grant (ISC3GM113728-01) at North Carolina A & T State University. We would like to thank Dr. Jagannathan Sankar of ERC director, Dr. Sergey Yarmolenko for mechanical testing guidance, Dr. Boyce Collins for micro-CT comment, and Dr. Guang-Ling Song for suggestion of the this study.

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