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Influence of circumferential notch and fatigue crack on the mechanical integrity of biodegradable magnesium-based alloy in simulated body fluid

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Abstract

Applications of magnesium alloys as biodegradable orthopaedic implants are critically dependent on the mechanical integrity of the implant during service. In this study, the mechanical integrity of an AZ91 magnesium alloy was studied using a constant extension rate tensile (CERT) method. The samples in two different geometries i.e., circumferentially notched (CN), and circumferentially notched and fatigue cracked (CNFC), were tested in air and in simulated body fluid (SBF). The test results show that the mechanical integrity of the AZ91 magnesium alloy decreased substantially (~50%) in both the CN and CNFC samples exposed to SBF. Fracture surface analysis revealed secondary cracks suggesting stress corrosion cracking susceptibility of the alloy in SBF.

Key words*:* magnesium alloys; biodegradable implant; mechanical integrity; stress corrosion cracking; simulated body fluid

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INTRODUCTION

Magnesium has been identified as a possible metal to replace current implant materials for use as biodegradable orthopaedic implants. The degradation tendency of magnesium in physiological environment and the non-toxic soluble products that tend to excrete harmlessly with the urine and by the intestine[1,2] makes magnesium very attractive for biodegradable implant applications. Magnesium possesses mechanical properties similar to bone and is further essential to the human metabolism.[2,3] In spite of these advantages, applications of magnesium implants are not common, primarily because magnesium degradation is unacceptably high in physiological condition, i.e., pH-levels of 7.4 - 7.6 and high chloride concentration, and hence the implant materials will dissolve long before the expected service life. [2,4]

The development of magnesium-based alloys for implant applications has been increased significantly for the past few years.[4-6] The in-vivo and in-vitro corrosion behaviour of different magnesium alloys have been evaluated. [4-7] Witte et al.[4,10] reported that AZ91 magnesium alloy implants caused no significant harm to their neighbouring tissues and also exhibited good biocompatibility.

For orthopaedic implant applications, the in-service mechanical integrity of the implant materials especially for screws and plates is a critical factor,[11,12] besides adequate degradation resistance in human body fluid and biocompatibility.[2] Though biodegradable implants are allowed to dissolve, the material would still need to possess the desired strength to support and protect the healing tissue. Implant devices such as screws and pins made of stainless steel AISI 316 have been shown to be affected by stress-corrosion under in-vitro and even more severe under in-vivo conditions.[11,12] Fatigue failures of orthopaedic implants in humans are also reported in literature.[13,14] Stresses when assisted by corrosion may result in sudden catastrophic/premature cracking, viz. stress corrosion cracking. This phenomenon is particularly relevant for biodegradable orthopaedic implants made of magnesium-based alloys. It is important to note in this context that AZ series magnesium alloys are susceptible to stress corrosion cracking in chloride containing environment.[15-18]

Our recent in-vitro studies on the mechanical integrity of various magnesium alloys using smooth tensile samples showed no significant losses in the mechanical properties, but revealed signs of stress corrosion crack initiation.[6,7] It is important to note that the geometry of the implant materials and especially that of screws is not smooth, hence it is necessary to study the mechanical integrity of the material with geometry similar to the implants used in orthopaedic applications. In addition, implant materials experience both tension and compression stresses, and since implants have shown fatigue failure it is also important to look at the influence of fatigue cracking on the mechanical integrity of the alloy in a physiological environment.

In this study, AZ91 magnesium alloy with two different geometries i.e., circumferentially notched (CN), and circumferentially notched and fatigue cracked (CNFC), were tested under constant extension rate tensile (CERT) method in air and in simulated body fluid (SBF) to evaluate the mechanical integrity of the alloy in physiological environment. Fracture surface analysis was carried out using scanning electron microscope to understand the failure mechanism.

MATERIALS AND METHODS

AZ91 magnesium alloy (extruded) was used in this study due to its biocompatibility and the extensive literature on the stress corrosion cracking of AZ series alloys under various microstructural and environmental conditions.[7,15-18] The composition of the alloy determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) is listed in Table 1. For microstructural examination using optical microscopy, specimen was prepared by standard metallographic procedure and was etched in a solution containing 3.5 g picric acid, 6.5 ml acetic acid, 20 ml water and 100 ml ethanol.

For mechanical integrity evaluation, samples with two different geometries were used: (i) a circumferential 60º V-notch was produced in the centre of the gauge section of a typical tensile sample (hereafter denoted as CN), and (ii) ahead of a circumferential 60º V-notch a uniform fatigue crack was produced (hereafter denoted as CNFC). Schematic drawings of the test samples with different geometries are shown in Figs. 1a and b. In the CNFC samples, the fatigue cracks were produced ahead of the notched area by subjecting circumferentially notched samples to a controlled fatigue in a rotating-bending machine. A peak bending stress of 120 kPa was applied to the rotating sample for ~ 5mins.

In-vitro mechanical integrity studies were carried out on CN and CNFC samples in simulated body fluid (SBF) using constant extension rate tensile (CERT) tests. The chemical composition of the SBF is given in Table 2. The solution was buffered with 2-(4-(2-hydroxyethyl)-1-piperazinyl) ethanesulfonic acid (HEPES) to maintain a physiological pH of 7.4. A schematic diagram of the experimental set-up is shown in Fig. 2. The cylindrical cell was constructed from Perspex with inlet and outlet plugs to allow circulation of the SBF. The test sample was sealed at the base of the cell via an O-ring and silicone sealant to avoid any possible leakage. The SBF was heated in a water bath and circulated through the test cell using a submersible pump. The temperature of the SBF in the cell was maintained at 36.5 ± 0.5ºC during the experiments.

In the CERT test method the samples were pulled at a cross-head speed of 0.001 mm/min until fracture. Each experiment was conducted in triplicate to ensure the reproducibility of the results. For comparison, the tests were also carried out in air at the same cross-head speed. After the completion of the tests, the fracture surfaces were cleaned with chromic acid and distilled water and were then examined under scanning electron microscope (SEM).

RESULTS

The optical microstructures of AZ91 magnesium alloy are shown in Figs. 3a,b. Secondary phase particles along the grain boundaries and in the grains can be seen in Fig. 3a. Literature suggests these particles are mainly composed of magnesium and aluminium corresponding to $Mg_{17}Al_{12}$.[19] A higher magnification reveals that the particles on the grains exhibit a coupled-eutectic structure (Fig. 3b).

The stress vs time graphs obtained from CERT tests for the CN and CNFC samples are shown in Fig.4. The CN samples in air had a failure stress of 340 MPa, and the time to failure was ~5400 mins, whereas in the SBF the samples showed a significant loss of about 55% in the failure stress. The specimen failure stress decreased to 150 MPa, and the time to failure decreased to ~3400 mins. In the case of the CNFS samples, the failure stress in air was 240 MPa and the failure time was 8400 mins, while in the SBF the samples failed at 100 MPa and the failure time was ~ 5000 mins. The samples underwent a loss of 58% of its strength.

The photographs of the CN and CNFC samples which failed in the CERT tests in air and in SBF are shown in Figs.5 a,b. Comparing the sample tested in air to that tested in SBF, it is clearly seen that the samples exposed to SBF underwent moderate surface corrosion. Though the CNFC samples were exposed to SBF for a longer period of time (as can be noted from Fig. 4), the surfaces of the CNFC samples show a similar extent of corrosion as those of the CN samples.

The fracture surface of a CN sample tested in air is shown in Figs. 6 a and b. The overall fracture surface shows a fibrous ductile nature of failure (Fig.6a). A higher magnification reveals dimples and ductile tearing (Fig. 6b). The fracture surface of a sample tested in SBF is shown in Figs.6 c and d. A localized attack along the machine notched portion of the sample is evident in Fig. 6c. It can be noticed in Fig. 6d that the localized attack initiated in the machine notched area and propagated into the fractured zone. The fractured zone reveals secondary cracks.

Figs.7 a and b show the fracture surface of a CNFC sample tested in air. Three regions are clearly visible in Fig. 7a, i.e., the machined notch (MN), the fatigue cracked (FC), and the fractured surface (FS). A clear boundary between the fatigue cracked and the fracture surface can be seen in Fig. 7b. The fatigue cracked region shows striations, a common feature of fatigue failure. However, the fractured surface shows ductile features revealing dimples. The fracture surface of a CNFC sample tested in SBF is shown in Figs.8 a-d. The over all view of the fractured sample shows some localized attack on the machined notched portion and even on the fractured surface (Fig. 8a). Interestingly, no visible localized attack is evident in the fatigue crack region, however, it appears to be slightly different than that of the air tested sample (see Figs. 8b, 7b), probably due to some surface corrosion. On the fractured surface, two regions can be observed, (i) with intense localized attack, and (ii) showing no evidence of localized attack. Having a closer look at the localized attack region, secondary cracks can be observed (Fig. 8d).

DISCUSSION

In order to quantify the loss of mechanical strength due to the exposure of the samples to SBF, a mechanical integrity index (I_{MI}) was calculated which is the ratio of the failure stress of a sample tested in SBF to the failure stress of a sample tested in air. Hence, a higher I_{MI} suggests better performance of the sample in SBF. In Table 3, the calculated I_{MI} for the CN and CNFC samples and, for comparison, the I_{MI} of smooth tensile specimens[16] are given. It is clearly seen that, introducing a notch in the sample, substantially brings down the mechanical integrity of the alloy in SBF. The smooth specimen showed an index of 0.83 whereas the CN and CNFC samples showed indices of 0.44 and 0.41, respectively (Table 3). It is noted from the I_{MI} that the introduction of a fatigue crack has not caused a further significant loss on the mechanical integrity of the alloy. However, it cannot be concluded that fatigue cracks have no influence on the mechanical integrity of the alloy in SBF, simply because the I_{MI} of the notched sample is itself very low.

Comparing the fracture surfaces of the CN and CNFC samples tested in SBF, the common features observed are the secondary cracks, which suggest that the alloy underwent stress corrosion cracking. Though it is difficult to state that the loss in mechanical integrity in SBF is solely due to stress corrosion cracking because of the general corrosion of magnesium alloy in SBF, it can be said that stress corrosion cracking played a significant role from the observation of secondary cracks in the fractured surfaces. The other issue is that the question why such a loss in mechanical integrity was not observed in the testing of smooth tensile samples under similar environmental condition.[17] Typically an incubation period exists for any localized corrosion to initiate on the smooth surface of the sample. In fact, localized corrosion region acts as a crack initiator. It is reported that calcium phosphate deposits on magnesium and its alloys when exposed to SBF. [7,20] The formation of calcium phosphate film would definitely affect the crack initiation process and subsequent crack propagation. In the case of smooth tensile samples, the kinetics of film formation could be sufficient to slow down the crack initiation and thereby the propagation. However, in the CN and CNFC samples the pre-existing crack propagates much faster than the film formation and hence the film formation has no significant effect on the mechanical integrity.

It is reported in literature that the differences in fatigue life of long-term orthopaedic implants made of stainless steel is in part due to the machining and manufacturing process.[12] The fatigue properties can be mainly influenced by the implant design, the material and the manufacturing process,[12] which seems to be also important for biodegradable magnesium implants. This study has shown the dependence of magnesium alloy mechanical integrity on the environmental condition and also the design of the specimen.

CONCLUSIONS

CERT tests of CN and CNFC samples and the analysis of the fracture surfaces obtained reveal the following points: (i) the mechanical integrity of the magnesium alloy AZ91 in SBF is dependent on the design of the specimen, (ii) a notch or crack substantially decreases the mechanical integrity of AZ91 magnesium alloy in SBF, and (iii) the fracture surfaces show evidence of stress corrosion cracking.

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FIGURE CAPTIONS

Figure 1. Schematic diagrams with dimensions of (a) circumferential 60º V-notch (CN) specimen and (b) circumferential 60º V-notch and fatigue cracked (CNFC) specimen.

Figure 2. Schematic diagram of the experimental set-up to evaluate the mechanical integrity of magnesium alloy samples in simulated body fluid at 36.5 ± 0.5ºC.

Figure 3. Optical micrographs of AZ91 magnesium alloy: (a) lower magnification shows cluster of secondary phase particles and (b) higher magnification reveals coupled-eutectic structure.

Figure 4. Stress vs time graph of CN and CNFC specimens tested in air and in simulated body fluid using constant extension rate tensile (CERT) method.

Figure 5. Photographs of failed (a) CN specimens and (b) CNFC specimens, tested in air and in simulated body fluid.

Figure 6. SEM fractographs of CN specimens tested in: (a, b) air and (c,d) simulated body fluid.

Figure 7. SEM fractographs of CNFC specimens tested in air: (a) overall view, and (b) the boundary of fatigued and fractured regions. (Note: MN-machined notch, FC-fatigue cracked, and FS – fractured surface).

Figure 8. SEM fractographs CNFC specimens tested in simulated body fluid (a) overall view, (b) fatigued region, (c) fractured region showing ductile features, and (d) fractured region showing secondary cracks.

TABLES

Table 1 Chemical composition of AZ91 magnesium alloy (wt.%).

Al	Zn	Mn	Fe	Si	Cu	Zr	Mg
9.06	0.61	0.23	0.005	0.01	0.001	<0.01	Bal.

Table 2 Chemical composition of simulated body fluid

Reagents	Amount
NaCl (g)	5.403
$NaHCO_3$ (g)	0.504
Na_2CO_3 (g)	0.426
KCl (g)	0.225
$K_2HPO_4{\cdot}3H_2O$ (g)	0.230
$MgCl_2{\cdot}6H_2O$ (g)	0.311
0.2 M NaOH (mL)	100
HEPES[a] (g)	17.892
$CaCl_2$ (g)	0.293
Na_2SO_4 (g)	0.072
1 M NaOH (mL)	15

[a] HEPES = 2-(4-(2-hydroxyethyl)-1-piperazinyl)ethanesulfonic acid.

Table 3 Mechanical integrity indices of AZ91 magnesium samples with different geometry.

Sample	I_{MI}*
Smooth sample [17]	0.83
Circumferentially notched sample	0.44
Circumferentially notched and fatigue cracked sample	0.41

* I_{MI} = Failure stress in SBF/ Failure stress in air