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Hydrogen Embrittlement of Biodegradable Magnesium

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Abstract

Magnesium alloys are increasingly used in biomedical applications as temporary implants in the human body. The degradation behaviour of magnesium in physiological environments, in combination with the tendency of the corrosion products to be harmlessly dissolved and excreted with the urine, make magnesium very attractive for temporary implant applications. One of these applications is the use of the material for making coronary stents. Such applications are, on the other hand, critically dependent on the mechanical integrity of the implant during service. A number of recent studies have evaluated the in-vivo and in-vitro corrosion behaviour of magnesium and its alloys, and the ongoing research seeks to provide a fundamental understanding of the factors that influence their bio-degradation and environmental failure and to expand this understanding through experimental evidence. In this paper, the propensity of the magnesium alloys AM30 and WE43 to hydrogen embrittlement and to corrosion fatigue was studied using constant extension rate tensile tests on fatigue pre-cracked compact specimens and corrosion fatigue tests on tubes which are typically used for the production of stents and which were tested in simulated body fluid.

Introduction

Magnesium alloys are becoming increasingly viable for biomedical applications as biodegradable, i.e., temporary, implants in the human body [1-5]. A number of recent studies have evaluated their in-vivo and in-vitro corrosion behaviour [6-10]. The degradation behaviour of magnesium in physiological environments, in combination with the tendency of the corrosion products to be harmlessly dissolved and excreted with the urine, make magnesium very attractive for temporary implant applications [11]. Magnesium alloy implants cause no significant harm to their neighbouring tissues and also exhibit good biocompatibility [12,13].

The mechanical properties of magnesium are closer to those of human bone than those of other metallic materials and magnesium is essential to the human metabolism [2, 14]. In spite of these advantages, applications of magnesium implants are not common, primarily because magnesium degradation is unacceptably fast in physiological conditions and hence the implant materials will dissolve long before the end of the expected service life [15]. Thus, ongoing research is aimed at developing a fundamental understanding of the factors that influence the bio-degradation and environmental failure of magnesium alloys and to expand this understanding through experimental evidence.

For many implant applications, in particular for orthopaedic applications, the structural integrity of the implant component is a critical factor, in addition to adequate corrosion resistance and biocompatibility [2]. Although biodegradable implants are allowed to dissolve, the material has to retain the desired strength at least until it has served its purpose.

Hydrogen-induced-cracking (HIC) of magnesium alloys has been discussed in a number of publications. It is generally accepted that hydrogen plays a major role in the stress corrosion cracking (SCC) behaviour of magnesium alloys [1,16-18]. Earlier studies showed that magnesium

alloys such as AZ31, AZ80, QE22 and ZE41 are susceptible to SCC and hydrogen embrittlement even in distilled water [1,19]. Stresses in combination with corrosion may result in sudden catastrophic/premature cracking due to hydrogen embrittlement, a phenomenon which can also be of relevance for biodegradable implants.

Experimental Details

The magnesium alloys AM30 and WE43 were investigated in this study. For preliminary SCC studies, compact specimens, C(T), were machined from large extrusions of both these materials with the chemical composition given in Table 1. The specimens were cut such that the crack propagation direction was parallel with the extrusion direction. Corrosion fatigue (CF) tests were performed on small tubes of about 100 mm length, 1.6 mm diameter and 0.2 mm wall thickness which had been produced WE43 material only.

Table 1. - Chemical composition in wt-% (average values from optical emission spectroscopy,)

designation	Al	Mn	Zn	Fe	Cu	Ni	Si	Nd
AM30	2,93	0,397	0,006	0,0033	0,0009	0,0006	0,0163	0,0000
WE43	0,0133	0,01	0,07	0,00259	0,00375	0,00908	<0,00005	2,64

Ca	Sn	Ag	Zr	Ce	La	Y	Pr	Pb	Rest Mg
0,0007	0,0000	0,0000	0,0000	0,0009	0,0000				96,00
0,0215	0,0045	0,00366	0,202	0,0213	0,0866	4,00	0,137	0,141	92,64

In the preliminary SCC tests on C(T) specimens the SCC test environment consisted of double-distilled water. Control tests were carried out in laboratory air previously shown to be inert [16-18]. The specimens had a thickness, B, of 7.5 mm, a notch depth of 18 mm and were fatigue pre-cracked to a/W ≈ 0.5 (where the width of the specimens, W, was 40 mm) prior to each test. SCC testing was performed under Constant Extension Rate Tensile (CERT) conditions in which the applied tensile loads were increased continuously, with the extension measured using a clip-on gauge at the crack mouth, i.e., the crack mouth opening displacement, CMOD [19]. The constant extension rates d(CMOD)/dt used were 1 and 100 μm/h, and crack initiation and extension were measured using a pulsed DCPD method which has been described in detail elsewhere [20]. The tests were evaluated according to linear elastic fracture mechanics methodology, i.e. the stress intensity factor K was calculated at the onset of crack extension using:

$$K = \frac{F}{B\sqrt{W}} \frac{(2+a/W)}{(1-a/W)^{1.5}} [0.886 + 4.64a/W - 13.32(a/W)^2 + 14.72(a/W)^3 - 5.6(a/W)^4] \quad (1)$$

where F is the load at crack initiation, W the ligament and a the initial crack length.

The CF tests were performed in simulated body fluid (SBF) and, for reference, also in laboratory air. Testing was performed in an electromechanical fatigue test apparatus at loading frequencies of ~ 20 Hz and R-ratios of ~ 0.1. The loading range of interest which was applied in these tests corresponded to cyclic stress levels from 40, 60 and 80 MPa, respectively.

Results

In Fig. 1 the results of the SCC tests on the pre-cracked C(T) AM30 specimens are displayed. The values of the stress intensity factor, K_I, calculated according to Eq. (1) are plotted as a function of the CMOD up to the point at which crack initiation occurred, detected by a sharp increase in DCPD signal. Although the overall slopes of the curves appear to some extent similar, it is obvious that in distilled water, i.e. under the condition of hydrogen embrittlement, the cracks initiated at much lower values of the CMOD than in the reference tests in air. In the tests performed at an extension rate of 1 µm/h cracking was observed after less than 0.5 mm increase in CMOD, whereas in a specimen tested in air at the same extension rate cracking occurred only after reaching CMOD values in the order of 1.8 mm. At the higher one of the two extension rates, i.e., at 100 µm/h, the fracture behaviour was obviously not influenced by the respective test environment, even in distilled water the mechanical rupture had overridden the degradation effect caused by hydrogen uptake.

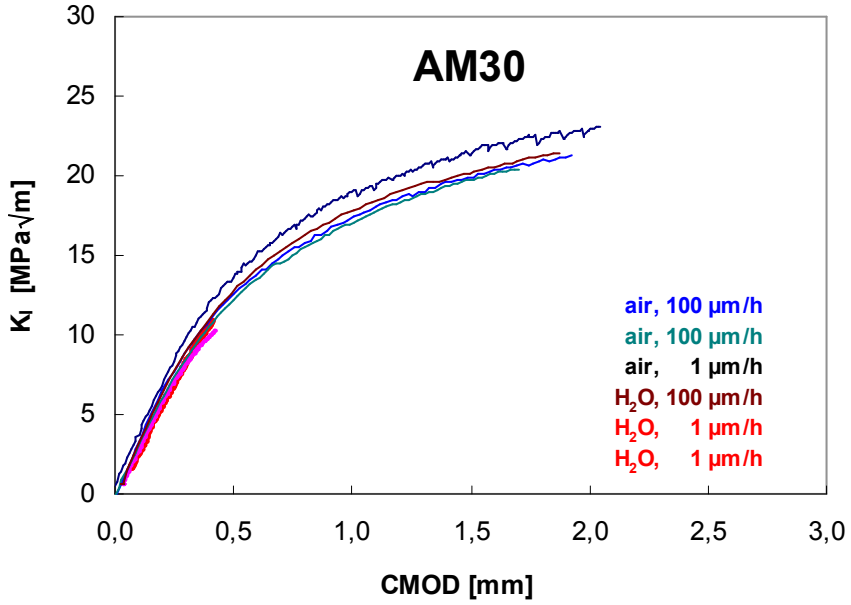

Fig. 1 - K vs. CMOD curves in laboratory air and in distilled water measured on AM30.

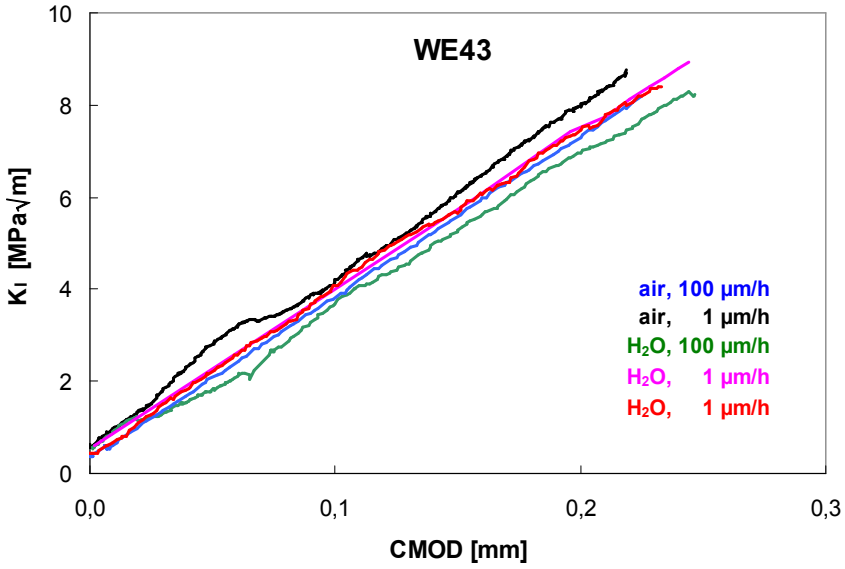

Fig. 2 - K vs. CMOD curves in laboratory air and in distilled water measured on WE43.

Fig. 2 shows the K_I versus CMOD curves for WE43 measured in distilled water and in laboratory air. There was little difference between K_{Ic}-values for WE43 samples tested in distilled water and laboratory air or between those tested at different extension rates. However, although WE43 did not exhibit a reduction in apparent fracture toughness due to exposure to distilled water, the K_{Ic}-values for WE43 are still considerably lower than those for AM30, as can be seen from the comparison of the two materials shown in Fig. 3

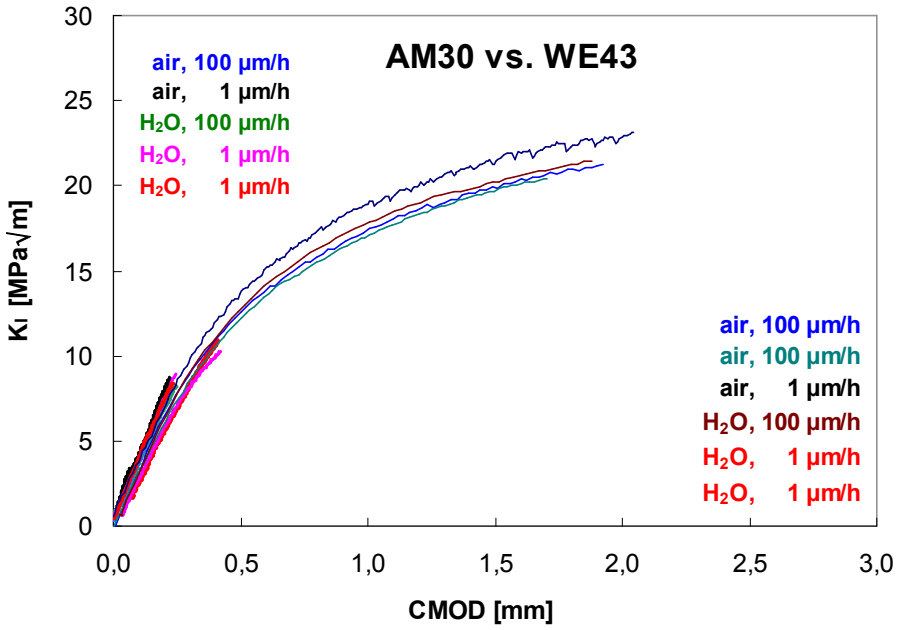

Fig. 3 - Comparison of the K vs. CMOD curves for AM30 and WE43.

The corrosion fatigue tests of the WE43 stent tubes revealed that the material was fairly sensitive when being tested in simulated body fluid, SBF, environment. Unlike the specimens which were tested in laboratory air and which sustained more than 10^7 cycles without failure, irrespective of the applied load, the specimens tested in SBF failed prematurely in the manner shown in Fig, 4. As is indicated in this figure, the tests in SBF were performed in triplicate manner at each of the three load levels.

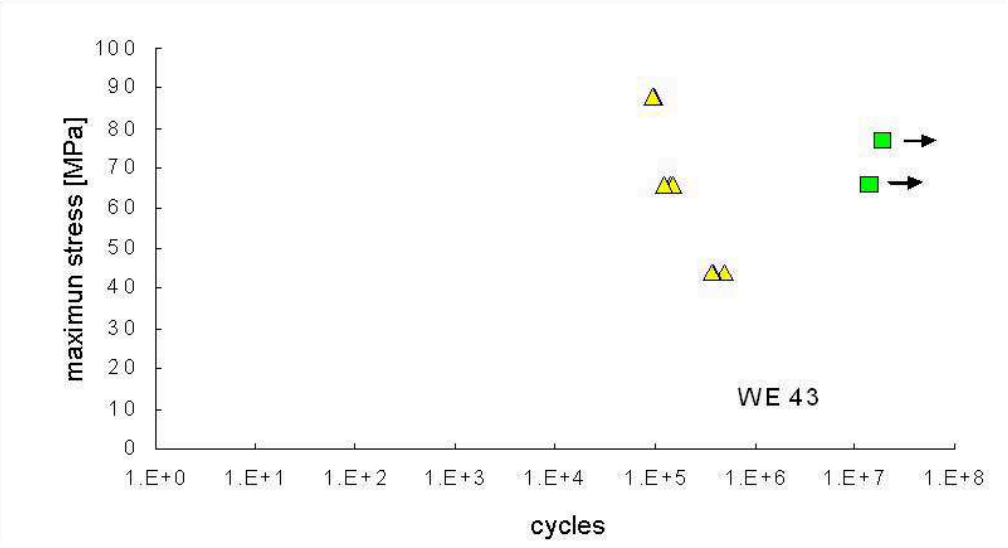

Fig.4 - Results of F testing of tubes for manufacturing stents in SBF (triangles, 3 tests at each load level) and in air (squares), material WE43.

The SEM pictures of one of the tubes of this material which were CF tested in SBF at a cyclic stress level of: 40 MPa does not reveal a non-ambiguous reason for the failure after only ~400 000 cycles. It can be assumed that this failure was greatly influenced by the specific production process of the tubes comprising a number of subsequent drawing steps and introducing hydrogen into the material. The hydrides thus formed may have been the major reason for the premature failures of the material.

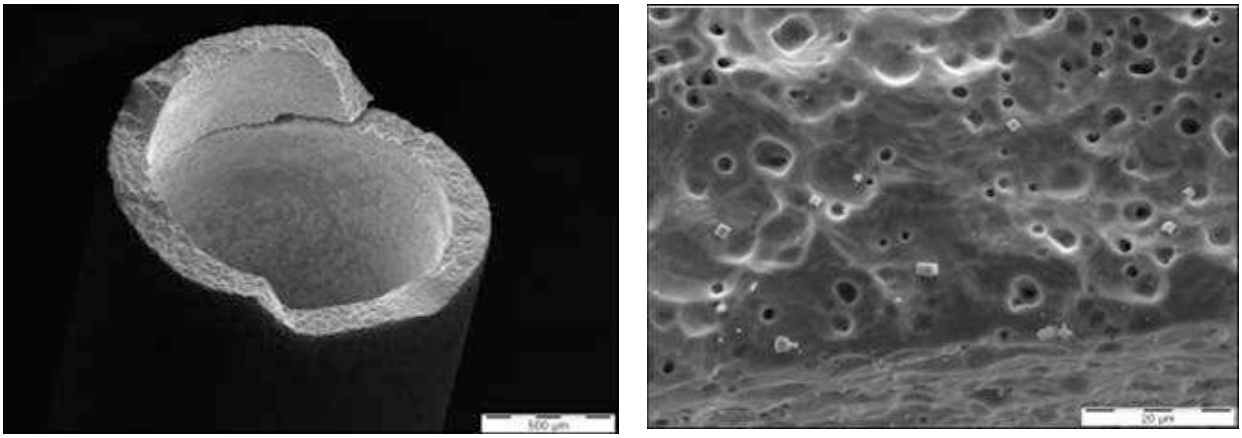

Fig.5 - SEM pictures of a tube which was CF tested in SBF at a cyclic stress level of: 40 MPa and failed after ~400 000 cycles (material WE43).

Conclusions

CERT tests on pre-cracked C(T) specimens of the magnesium alloys AM30 and WE43 revealed that the structural integrity of the magnesium alloy AM30 in distilled water was highly dependent on the applied extension rate, whereas this rate had no effect the alloy WE43, irrespective of whether the tests were performed in air or in distilled water. However, the K versus CMOD curves reveal the inherently higher brittleness of the WE43 alloy. CF tests on WE43 alloy in SBF show the high propensity of this material to environmental cracking in this biological environment which was potentially caused by the complicated production process of these tubes. This high propensity of the WE43 tubes to CF in SBF environment has in the meantime been overcome by changes in the alloy composition used and in the production process of the tubes.

Summary

The propensity of the magnesium alloys AM30 and WE43 to corrosion and hydrogen embrittlement was studied using constant extension rate tensile tests on fatigue pre-cracked compact specimens and corrosion fatigue tests on tubes which are typically used for the production of stents and which were tested in simulated body fluid.

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