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Influence of stress on the degradation behavior of Mg LAE442 implant systems

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Abstract

In this paper the performance of a magnesium based implant system is analyzed. A special emphasis is placed on the impact of stress on the corrosion behavior of the magnesium alloy. An implant system containing a plate and 4 corresponding screws is machined from Mg LAE442. Its corrosion behavior is tested in-vivo in New Zealand White Rabbits for 6 and 12 weeks of implantation. The plate is monocortically fixated on the medial tibia. At the interface between screw and plate increased corrosion is observed. This phenomenon is stronger on the caudal side of the screw. Parallel to the in-vivo test the influence of stress load on the corrosion rate is analyzed for LAE442 in in-vitro tests. Compressive load is applied on cylindrical specimens in axial direction and the corrosion rate is measured in 0.9 wt% NaCl solution by eudiometry and mass loss. Additionally rectangular samples are bent to apply tensile stress on the surface. A drop of 5 wt% NaCl is deposited on the surface and the corrosion is evaluated by microscopic images. It is shown that stress essentially influences the corrosion rate. While tensile stress decreases the corrosion, compressive stress leads to higher corrosion rates.

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1. Introduction

In osteosynthesis implants made of biodegradable materials are favorable. In contrast to permanent implants made of titanium alloys or chirurgical steel they dissolve in the human body after a certain period of time. This reduces the risk of infections and allergic reactions. Furthermore, a secondary surgery to remove the implant after the bone is healed can be avoided. Thereby, the risk for the patient and the associated costs for the healthcare system are omitted. Among resorbable implant materials magnesium alloys, in particular, exhibit favorable mechanical properties. The Young's modulus of magnesium is higher but still close to the Young's modulus of the human cortical bone [1]. This provides sufficient stability for load bearing implants, but avoids weakening of the bone due to stress shielding [2]. Ideal support is supplied by implants whose degradation induced loss in stability is matched by the increasing stability of the healing bone. Therefore, it is of great interest to control the corrosion rate of the implants. This can be done by adjusting the composition and the microstructure of the material and by tuning the surface integrity of the machined implants [3]. Special challenges arise when implant systems containing two or more parts are used. At the contact area the involved parts are exposed to high stress. These might influence the local corrosion behavior of the implants at these areas. A great part of the stability of implant systems

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mainly depends on the contact between the involved components. Therefore, it is important to understand to which extent the corrosion kinetics of the implant material is affected by stress.

To study the corrosion properties of implant systems a bone plate with corresponding interlocking screws has been machined from magnesium LAE442 and has been tested in-vivo in a pilot study in New Zealand White Rabbits. Analytical evaluation of the implants is done post-mortem by optical and electronic microscopy. In addition to that the influence of compressive and tensile stress on the corrosion rate of LAE442 samples is analyzed by in-vitro experiments using NaCl-solution.

2. Experimental

2.1. Material

The in-vivo and in-vitro experiments presented in this paper are performed with the magnesium alloy LAE442. LAE442 (Mg 90 wt%, Li 4 wt%, Al 4 wt%, RE 2 wt%) was manufactured by gravity die-casting using elements obtained from Magnesium Elektron UK (magnesium, AE42 master alloy), Chemetall GmbH (lithium) and Hydro Aluminum Deutschland GmbH (aluminium). The alloys were formed with the corresponding elements by melting at 750 °C in a steel crucible and stirring for 30 min. Here, due to its high reactivity and low melting point, lithium was added two minutes prior to stirring. The entire alloy casting process was carried out under a protective argon atmosphere. Cast billets with a diameter of 120 mm and a length of 300 mm were subsequently hot extruded to obtain a fine-grained microstructure with desired mechanical and corrosive properties. Extrusion was carried out by means of direct extrusion in a 10 MN extruder fabricated by SMS Meer. The extrusion die, with orifice diameter of 10 mm, and recipient was heated to a temperature of 320 °C. To create the LAE442 rods, the cast billets were inserted into the extruder and pressed through the extrusion die with a profile velocity of 1 mm*s^{-1} and a resulting maximum force of 9 MN. The extrusion ratio of the deformation was 16.

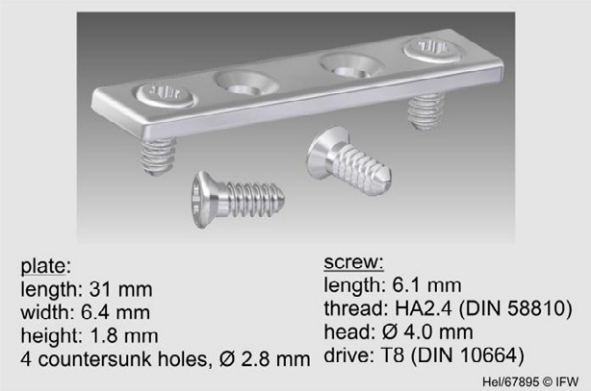

Figure 1. The displayed model represents the magnesium based implant system for in-vivo tests on New Zealand White Rabbits.

2.2. Implant system for in-vivo tests

For in-vivo-tests an implant system containing a plate and corresponding interlocking screws is machined. In figure 1 a CAD-model of the system and the corresponding dimensions are shown.

Two adult female New Zealand White Rabbits are used for in-vivo tests. The animal experiments carried out in this study were in accordance with a protocol approved by the ethic committee in charge as well as with § 8 of the German Animal Welfare Act. They were legitimized by the Office for Consumer Protection and Food Safety under the approval number 33.14-42502-04-10/0106. General anesthesia, pain management and antibiotic treatment are performed as described before [4]. In each rabbit one implant of magnesium and additionally, one commercially available implant of stainless austenitic steel (1.4441LA) are implanted. The magnesium and the steel plate are monocortically fixated on the medial tibia of the rabbits left and right leg, respectively. After 6 and 12 weeks of implantation the rabbits are euthanized. Subsequently cross sections of the tibia are prepared using a band saw. On these slices the corrosion is evaluated with an optical and an electron microscope. Energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) measurements of the implants are used to identify the corrosion products.

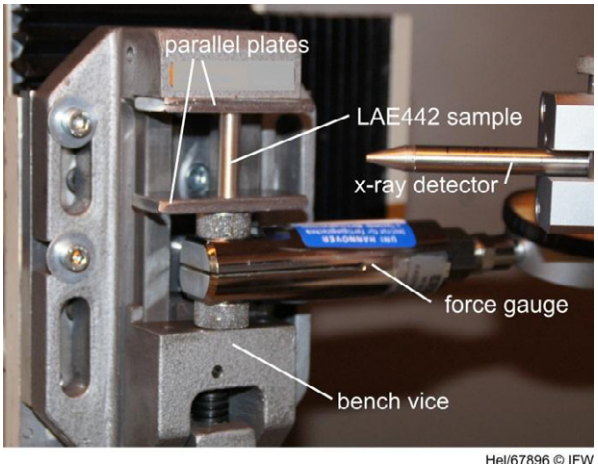

Figure 2. The stress in cylindrical LAE442 samples resulting from an external compressive load force in axial direction is detected by x-ray diffraction measurement.

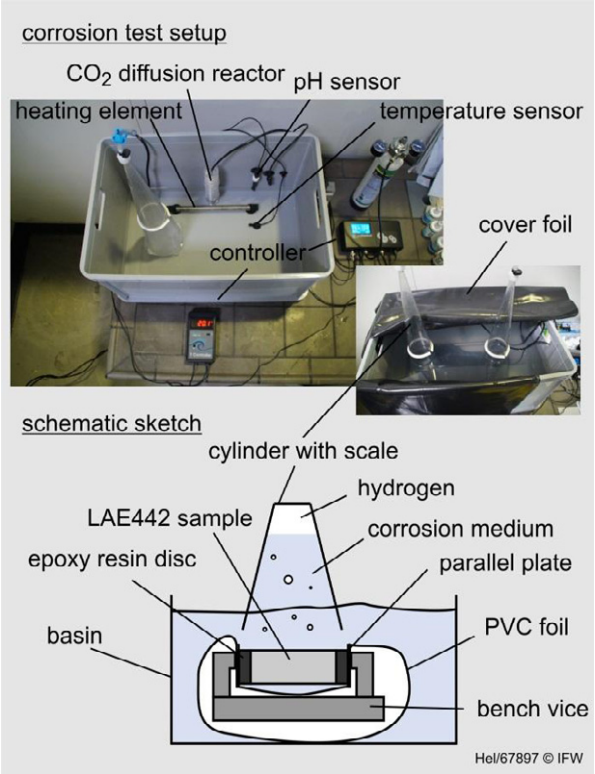

Figure 3. The in-vitro corrosion test setup allows the measurement of two samples one with and one without external load at the same time. The generated hydrogen is collected in scaled cylinders to determine the corrosion rate. During the corrosion tests the temperature and the pH value are kept constant.

2.3. Compressive load set-up

In order to analyze the influence of compressive stress on the corrosion kinetics external load is applied on cylindrical LAE442 specimens. The cylinders possess a length of $l = 30$ mm and a diameter of $d = 8$ mm. On these specimens external load is applied by using a bench vice. A force gauge is used to control the acting forces. To validate the calculated resulting stresses in the magnesium samples x-ray diffraction measurements are performed with a Seifert XRD 3000P with Cu/Ni radiation at $h\nu = 35$ keV (fig. 2). Surface qualities of the loaded and unloaded samples are analyzed by tactile measurements of the surface roughness.

The experimental setup for the corrosion measurement is shown in figure 3. The basin is filled with 0.9 wt.% NaCl solution which represents the salt content of the human organism. Two LAE442 specimens are placed at the bottom of the basin at the same time. Compressive load is applied on one specimen, the other remains unloaded. The temperature of the corrosion medium is kept constant at 37°C, the human body temperature, with the help of a temperature sensor and a heating element. Using CO_2 gas the pH value of the corrosion medium is kept within the range of 7.0 to 7.4. The corrosion rate of the magnesium specimens is measured by mass loss and by eudiometry. Mass loss measurement compares the weight of the specimen pre and post corrosion. For the latter the corrosion products are removed with chromic acid. Eudiometry uses the fact that magnesium corrodes through the release of hydrogen. According to the reaction equation of magnesium

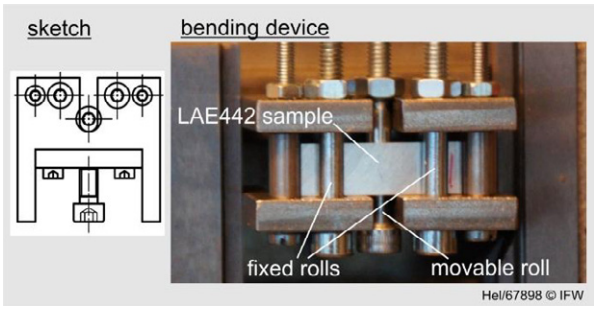

Figure 4. In order to apply tensile stress the samples are bend in a three point bending device. The displacement of the movable roll is adjusted with a screw at the bottom of the device.

$$Mg + 2\,H_2O \rightarrow Mg(OH)_2 + H_2 \qquad (1)$$

one mole of released hydrogen corresponds to one mole of corroded magnesium. To measure the released hydrogen, cylinders filled with the corrosion medium are placed above the magnesium specimen. Because of its low density the hydrogen accumulates at the top of the cylinders and its volume can be measured.

2.4. Tensile stress set-up

To apply tensile stress on LAE442 small rectangular samples ($l = 25$ mm, $w = 8$ mm, $t = 3$ mm) are machined. A bending device with two fixed and one movable cylinder is used to bend the magnesium samples (fig. 4). At the point of maximum elongation the stress is measured using X-ray diffraction. Furthermore the surface roughness is measured for all samples.

A well-defined drop of high concentrated salt solution containing 5 wt.% of NaCl is deposited in the area of maximum tension or rather the center of the sample for the unbent ones. The corrosion is observed with a video microscope. The corroded surface area is taken as measure for the degree of corrosion.

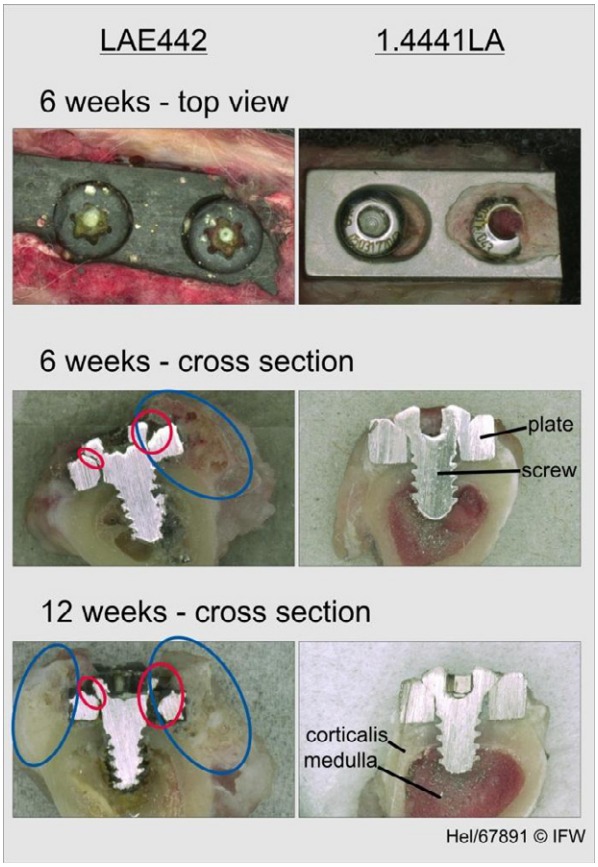

Figure 5. The microscope images are taken directly after euthanizing the rabbits. On the left hand side the magnesium implant system and on the right hand side the steel implant system is shown. The top four pictures are taken from the rabbit which was euthanized six weeks after the implantation and the two images at the bottom are taken from the rabbit which was euthanized after twelve weeks.

3. Results

3.1. In-vivo study on implant system

In this section the results of the in-vivo-tests of the implant system in New-Zealand-white-rabbits are described. In figure 5 optical microscope images taken directly after euthanizing the rabbits are shown. On the left hand side the LAE442 implants and on the right hand side the steel implants are shown. The first images compare the top view on both implants from the rabbit which was euthanized six weeks after the implantation. Below that the cross section of the bone-screw-plate-interface of the same implants are displayed. The images on the bottom show the same cross section for the implants of the other rabbit which was euthanized twelve weeks after the implantation.

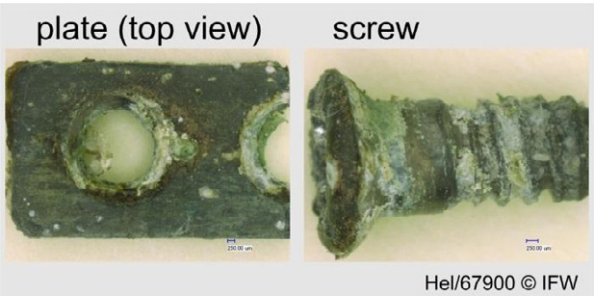

Figure 6. This microscope images are taken from the separated implants of the 6-weeks-rabbit.

The overall surface of the magnesium implant system is turned black. EDX analysis shows a carbon content of more than 60 at.% at these areas and in X-ray diffraction measurements no distinct reflections are found. This suggests that an amorphous organic film is adsorbed on the implant. White spots are scattered over the black film. According to EDX analysis they possess relatively high Ca and P contents. The reflections of the XRD measurement at these spots can be assigned to apatite ($Ca_5(Po_4)_3OH$). This is the base material of human bone. Thus the white spots are first signs of beginning bone formation on top of the plate. The microscope images of the cross section of the magnesium implants reveal that the corrosion is especially strong at the interface areas between plate and screw (red circle). In figure 6 the microscope images of the separated implants of the 6-weeks-rabbit are shown. XRD and EDX measurements on this materials indicate that this consists mostly of brucite ($Mg(OH)_2$). Scanning electron microscope (SEM) images show the microstructure of this material (fig. 7). The corrosion on the interface area between plate and screw is especially strong at the caudal side of the implants of both rabbits.

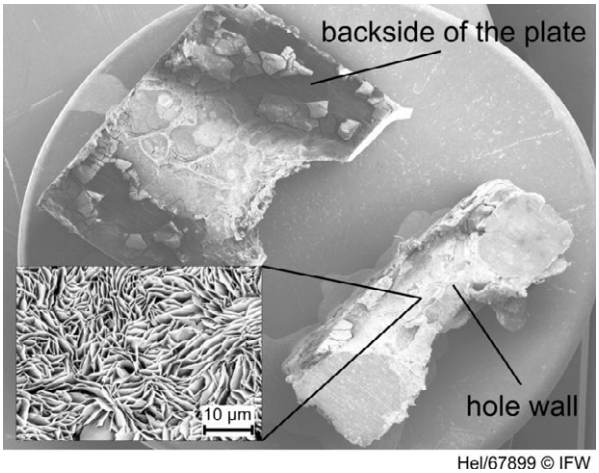

Figure 7. These SEM images reveal the structure of the corroded interface area.

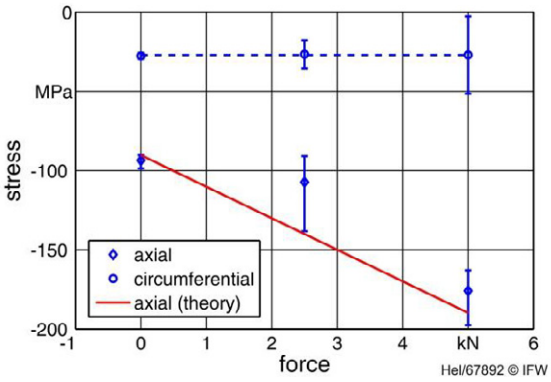

Figure 8. The stress on the cylindrical LAE442 specimens is measured by X-ray diffraction with respect to the applied load force in axial direction.

It is possible that asymmetric stress caused by the natural geometry of the rabbit tibia results in locally different corrosion rates.

In addition to the increased corrosion new bone is forming around the plate. In figure 5 the areas of bone formation are encircled in blue. The bone formation and remodeling processes are strongly increased with ongoing time of implantation. The excessive bone formation is a side effect of the bioactivity of the degrading magnesium alloy and in contrast appears only marginally around the steel implant. The bone formation and remodeling correspond to the increased corrosion. It can be expected that a reduction of the corrosion rate will also reduce the bone reactions.

3.2. In-vitro analysis of compressive load

On the cylindrical specimens described above 2.5 kN and 5.0 kN load is applied in axial direction. The corresponding stress measured by X-ray diffraction is shown in figure 8. Each measurement was repeated for 3 different samples. The measured stress in circumferential direction is not affected by the applied axial load. In axial direction the relatively high stress is found without applying any force. This is due to residual stress present in the extruded material. Applying axial load on the specimens implicates additional stress to the residual stresses. Since the cylinders have a diameter of 8 mm a load force of 5 kN should result in 99.5 MPa additional compressive stress. This theoretical value is indicated by the red line in figure 8. The experimental date matches the theoretical curve within the given error interval.

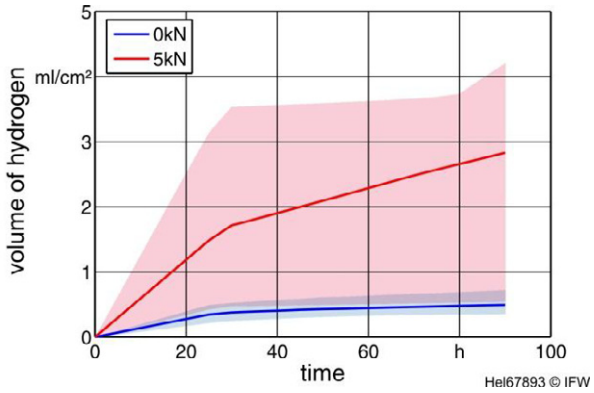

Figure 9. The solid lines indicate the mean values of the eudiometry measurement for LAE442 samples with 0 kN and 5 kN applied load force. The confidence interval is given by the light coloured areas.

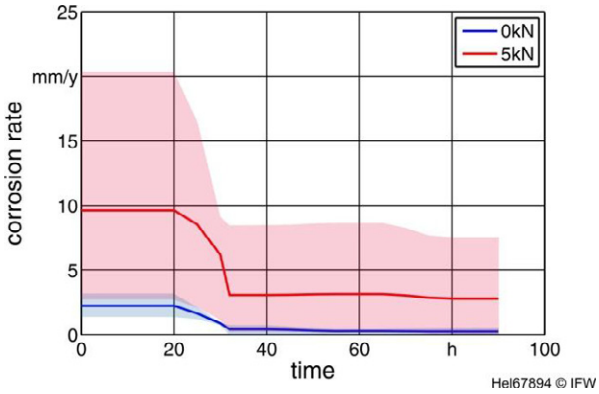

Figure 10. The corrosion rate is calculated from the eudeometry data and the correction factor from mass loss measurements.

The surface roughness was measured in 19 line scans on 4 unloaded samples and 26 line scans on 5 samples with 5 kN load force. Resulting mean values were R_a = (2.0 ± 0.2) µm for both the loaded and the unloaded specimens. These results indicate that the external load does not affect the surface roughness.

According to the measurement setup shown in figure 3 the corrosion performance of one stress-free sample and one sample with 5 kN external load force is measured at the same time. In figure 9 the hydrogen volume determined with respect to the corrosion time is displayed. The solid lines represent the mean values of three test series and the light colored areas mark the interval of minimal and maximal values. For one test series the corrosion rate is additionally measured by the mass loss of the samples as described in 2.3. According to equation 1 one mL of evolved hydrogen per cm² surface area and hour corresponds to a corrosion rate of 55 mm/y. Using this relation the corrosion rate given by mass loss measurement can be compared with the corrosion rate given by eudiometry. The factor by which the corrosion rate of the loaded sample is enhanced is up to 2% the same for both methods but the absolute value for the corrosion rate is significantly higher when calculated by mass loss. This effect was observed previously for corrosion measurements on different

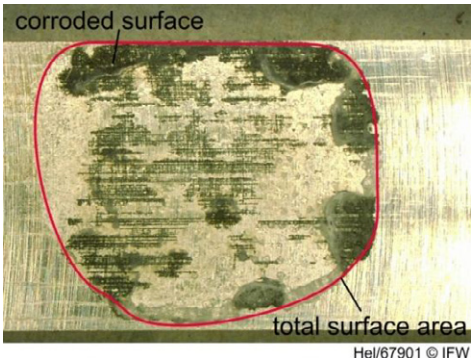

Figure 11. The ratio of the corroded surface (black) and the total surface area is taken as measure for the degree of corrosion.

magnesium alloys [3,5]. Major parts of the hydrogen gas are dissolved in the corrosion medium, which is why not all the evolved hydrogen is measured. By comparing the corrosion rates of both methods a correction factor of 2.94 is derived. Using this and the above given relation the corrosion rate presented in figure 10 is calculated. The corrosion rate is significantly higher for the sample with applied compressive stress. For both specimens the rate is highest at the beginning of the measurement and successively decreases. This is due to the forming $Mg(OH)_2$ surface film which has a partly passivation effect on the sample. Although the error intervals of both curves overlap, the corrosion rate for the compressed samples is always at least 35% higher when each test series is evaluated separately.

3.3. Analysis of tensile stress

According to the set-up described in 2.4 tensile stress is applied on LAE442 samples. To assure a constant surface quality of the samples in a first step the surface roughness is measured with respect to the displacement d of the movable bending roll of the bending device. The results are shown in table 1.

Table 1. The roughness of the LAE442 samples is measured with respect to the displacement of the bending roll on the bending device.

***d* [mm]**	0	0.2	0.3	0.5	0.8
R_a [µm]	0.16	0.16	0.20	0.28	0.44

Basing on these measurements the samples are bent by 0.2 mm and the resulting stress is measured with X-ray diffraction. In the direction perpendicular to the bending roll the stress is increased from (-30 ± 20) MPa for the relaxed samples to (200 ± 5) MPa for the bent ones. Control measurements of the stress in the direction of the bending roll give stresses close to 0 MPa for all cases.

The corrosion is measured for 5 bent and 5 unbent samples. In figure 11 the resulting surface after the corrosion is shown for one sample. The ratio c of the black area to the total area which has been wetted by the corrosion medium is taken as a measure for the corrosion. The results are shown in table 2. Although the statistical error is very large there is a clear tendency towards reduced corrosion for the samples with applied tensile stress.

Table 2. The fraction c of the corroded surface area is measured with respect to the displacement of the bending roll.

***d* [mm]**	0	0.2
***c* [%]**	41 ± 24	21 ± 10

4. Discussion

The in-vitro experiments show that compressive stress increases the corrosion rate. In contrast to that tensile stress reduces corrosion. An explanation for this effect is that the corroded surface film ($Mg(OH)_2$) and the substrate material (mostly Mg) have a mismatch. The hydroxide film needs a larger volume than the magnesium in the implant. Therefore compressing the magnesium enhances the mismatch and stretching it reduces the mismatch. Pilling and Bedworth introduced in 1927 a criterion to evaluate the protective impact of covering layers [6]. The Pilling-Bedworth-ratio (R_{PB}) is defined as the ratio of the mole volumes of the oxide film and substrate metal. For $R_{PB} << 1$ tensile stress and for $R_{PB} >> 1$ compressive stress leads to enhanced surface-film-cracking and consequently increased corrosion. For Mg and $Mg(OH)_2$ the R_{PB} is 1.75. This approves the observed corrosion behavior. In the literature sometimes a R_{PB} of 0.81 is found for magnesium [7]. This value is obtained when the mole volume of MgO instead of $Mg(OH)_2$ is used. Since the in-vivo experiments clearly show a $Mg(OH)_2$ layer on the corroded surface it seems appropriate to use $R_{PB} = 1.75$ for in-vivo corrosion of magnesium implants.

5. Summary and outlook

In this paper first results of an in-vivo test of magnesium implant systems have been shown. Two New-Zealand White Rabbits were used for these tests. They were euthanized after 6 or 12 weeks of implantation respectively. Post mortem increased corrosion was found on the interface between plate and screw. This effect is more dominant for the implant system with longer implantation time. Parallel to the increased corrosion excessive bone forming and remodeling processes are present around the magnesium implant system. In in-vitro tests the impact of compressive and tensile stress on the corrosion rate is analyzed. While compressive stress increases the

corrosion rate tensile stress leads to reduced corrosion. These results explain the increased corrosion in the in-vivo tests. Since compressive stress acts at the contact areas of the implant parts the corrosion rate is locally increased.

In a next step we will work on implant systems with modified contact areas which might compensate this effect.

Acknowledgements

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