Doctoral Thesis

Biodegradable magnesium alloys for osteosynthesis alloy development and surface modifications

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BIODEGRADABLE MAGNESIUM ALLOYS FOR
OSTEOSYNTHESIS – ALLOY DEVELOPMENT AND
SURFACE MODIFICATIONS

A dissertation submitted to
ETH ZURICH

for the degree of
Doctor of Sciences

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Abstract

Magnesium and its alloys are interesting candidates for temporary implant applications in osteosynthesis, as magnesium is degradable, physiologically compatible and even stimulates bone growth. Degradable implants have the advantage that a second surgery for implant removal is not required. However, despite intense research going on in this field, there are so far no Mg-based degradable orthopaedic implants commercially available. It was the aim of this Ph.D. project to develop new Mg alloys with properties fulfilling the requirements of such implants. Thereby, the electrochemical (i.e. slow and homogeneous degradation), mechanical (i.e. high strength and moderate ductility) and biological performance (i.e. non-toxicity of the alloy) of the new material must be considered and optimised.

The first part of this thesis focuses on the improvement of the initial degradation resistance of a commercially available Mg–Y–RE alloy by various surface treatments. Heat treatments are a simple, but effective tool to reduce the initial corrosion rate, due to the formation of a protective surface oxide layer. Other than with polished samples, which corrode fast at the beginning and slow down with time, the degradation rate of oxidised samples is initially low, and increases with time and penetration of the surface layer. The corrosion behaviour depends on the heat treatment duration, which can be explained based on a depletion hypothesis. In a second approach plasma-electrolytic oxidised coatings were investigated. These porous ceramic oxides also reduce the initial corrosion rate. However, under static tensile uniaxial loading, which might arise when the material is used in a bone implant, stress corrosion cracking occurs and decreases the rupture life. The brittleness of such ceramic coatings, which can result in the formation of cracks in the coating upon implantation (e.g. bending of the implant) and thus diminished protective function, is a major issue. To come across this, in a further approach ductile metallic Zn coatings were electroplated. It was found difficult, however, to deposit homogeneous and pore-free Zn coatings due to the relatively high reactivity of the Mg substrate material. Thus, the initial degradation rate
is only slightly reduced, and as soon as the Zn coating is penetrated, galvanic corrosion occurs, which may drastically increase the corrosion rate.

In the second part of this thesis, an alloy development strategy to produce high-strength Mg alloys is presented. The design principles are based on grain refinement during casting and forming, as grain-boundary-strengthening is an effective way of improving the strength of Mg alloys. In addition, their influence on electrochemical and biological properties were considered when choosing the alloying elements. The newly developed Mg–Zn–Zr–Ca(–Yb) alloys exhibit high yield strength (yield stresses of up to 350 MPa) at moderate ductility (elongation to fracture >15%) in the as-extruded state. By heat treatments, the alloys’ properties can be tailored: the yield strength slightly decreases (yield stress of 230–315 MPa) while the ductility significantly improves (elongation to fracture >20%). The attractive mechanical properties are attributed to the small grain size, the incomplete recrystallisation and precipitation hardening. A limiting property of these new alloys for potential use as implant, however, is their still rather low corrosion resistance, which could not be significantly improved by surface treatments limiting their application as implant materials. But, adding Yb to Mg–Zn alloys has a great effect on the hot tearing susceptibility (HTS) during direct chill casting; the HTS is drastically decreased and no cracks form. This is explained by the reduction of the terminal freezing range by the addition of Yb and also Y.

In summary, the surface-heat-treated Mg–Y-RE alloy seems to be the most promising candidate for implant applications in osteosynthesis, due to its good electrochemical performance and its rather high strength. The newly developed alloys exhibit outstanding mechanical properties. Their degradation performance still exhibits optimisation potential, however.
Zusammenfassung


Reaktivität des Mg Substrats nicht möglich war, homogene und porenfreie Zn-Schichten abzuscheiden. Die anfängliche Abbaurate wird zwar reduziert, sobald aber die Schicht lokal durchdrungen wird, findet galvanische Korrosion statt, welche den Korrosionswiderstand herabsetzt.

Der zweite Teil dieser Arbeit befasst sich mit der Entwicklung von neuen hochfesten Magnesium-Legierungen. Die Legierungsentwicklung basiert auf Kornfeinung während der Herstellungsprozesse (Strangguss und nachfolgendes Umformen), da Feinkornbildung eine wirksame Methode ist, um gleichzeitig die Festigkeit und die Duktilität zu erhöhen. Sie beruht auf der geeigneten Wahl von Kornwachstums-hemmenden Legierungselementen, welche sich zudem auch positiv auf die elektrochemischen und biologischen Eigenschaften auswirken müssen. Die neu entwickelten Mg–Zn–Zr–Ca(–Yb) Legierungen weisen exzellente mechanische Eigenschaften auf. Im extrudierten Zustand beträgt die Streckgrenze bis zu 350 MPa bei einer Bruchdehnung von >15%. Mittels Wärmebehandlungen kann das Eigenschaftsprofil erweitert werden: die Festigkeit wird zwar etwas verringert (Streckgrenzen von 230–315 MPa), die Duktilität wird aber erheblich verbessert (Bruchdehnungen >20%). Dies wird dem Feinkorn, sowie der Ausscheidungs-Härtung und der unvollständigen Rekristallisation zugeschrieben. Eine Einschränkung dieser hochfesten Legierungen ist ihr noch relativ geringer Korrosionswiderstand, welcher auch nicht durch Oberflächenbehandlungen signifikant erhöht werden konnte, was deren Einsatz als Implantat ohne weitere Modifikation vorerst einschränkt. Ein weiterer grosser Vorteil der Zugabe von Yb (und auch Y) neben dem positiven Einfluss auf die mechanischen Eigenschaften ist jedoch, dass die hohe Heissrissneigung von Mg–Zn Legierungen während des Stranggusses markant reduziert wird, vorwiegend durch die Verringerung des letzten Erstarrungsintervalls.

Chapter 1

Introduction

1.1 Magnesium as a biodegradable implant material for osteosynthesis

Properties of magnesium

Magnesium and its alloys are commonly utilised as construction materials in light-weight applications in the transportation industry, due to their low weight, high specific strength and fast machinability [1]. However, magnesium is also considered a suitable candidate for biodegradable implants in osteosynthesis (the focus of this work) or other temporary medical applications because (i) it is physiologically compatible, (ii) it is biodegradable in the human body and (iii) it stimulates bone formation, e.g. [2-4]. In contrast to applications in the transportation industry, where corrosion is undesirable, in medical applications it is of particular advantage. But, an important issue to be considered is the generally high corrosion rate of Mg alloys, which can be modified by the choice of suitable alloying elements or by surface modifications. Thereby, care must be taken to only select elements, which are not harmful to the body.

Magnesium is an essential element in the human body; an adult body contains around 21–28 g Mg corresponding to approximately 1 mole of Mg, which is mainly found in the bone, muscle and soft tissue [5]. Excess magnesium is secreted in the urine [5]. Despite magnesium being needed by the human body in relatively large
amounts, the degradation of a Mg-based implant should not proceed too fast, especially immediately following implantation. Firstly, the implant needs adequate strength during the period after implantation until the tissue has sufficiently healed to carry the applied load; too fast corrosion might lead to early loss of implant stability. Secondly, gaseous hydrogen, which is produced during the degradation of Mg in aqueous solutions \( \text{Mg} + 2 \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \), and the pH increase associated with the corrosion process might further irritate the injured tissue. However, the hydrogen gas around the implant as seen in Fig. 1.1.1c disappears with time or can be removed by a puncture and was found to be “uncomfortable” rather than actually harmful [3]. Despite the relatively high corrosion rates magnesium has a positive influence on bone growth [2-4]; in an in vivo study more bone mass was found around a Mg pin compared to a biodegradable polymeric implant material (Fig. 1.1.1a, b) [3]. Moreover, in an in vitro study of an \( \text{Al}_2\text{O}_3 \) ceramic implant the adhesion with human bone-derived cells was improved, when \( \text{Mg}^{2+} \) ions were added to the surface, compared to non-treated samples [4].

![Figure 1.1.1: Fluoroscopic images of cross-sections of (a) a degradable polymer (polylactide) and (b) a Mg rod after 18 weeks in a guinea pig femur. It can be seen that Mg stimulates bone formation. I indicates the implant, P periosteal bone formation and E endosteal bone formation. (c) Subcutaneous gas bubble observed around the Mg implant. With time the gas bubble disappears. [3]](image)

Generally, degradable implants have the advantage that a second surgery for removal of the implant is not necessary, saving cost to the health system and being beneficial for the patient. In addition, degradable implants are also applicable in paediatric cases, where the body is still in a growth process and permanent implants would have to be changed to match growth. Moreover, the healing and remodelling
process of the injured tissue is stimulated by degradable implants due to a gradual load transfer from the implant to the tissue, as depicted in Fig. 1.1.2 [6]. After an injury the fractured bone needs support from the implant for healing. With time the implant degrades, its strength diminishes and, consequently, the load is (partially) transferred to the bone until at the end the tissue has healed and obtained its (full) strength while the implant has dissolved. The optimal degradation performance of a bioabsorbable orthopaedic implant is initially slow to provide mechanical integrity and increases with time once the injured tissue has healed sufficiently.

![Figure 1.1.2: Schematic diagram of the ideal change in strength over time of a degrading implant and a healing tissue [6].](image)

In contrast to other implant materials, magnesium has further advantages. Compared to available polymeric biodegradable materials used in osteosynthesis, Mg exhibits higher strength. Compared to permanent metallic implants, stress shielding (which emerges from the difference in stiffness/Young’s modulus between implant and bone and which diminishes the healing process, bone growth and implant stability) can be reduced or even avoided by the use of Mg [7]; the Young’s modulus of Mg (41–45 GPa) is closer to that of human bone (3–20 GPa) than other permanent implant materials, such as stainless steel (190–205 GPa), Ti (110–117 GPa) or a Co-Cr alloy (230 GPa) [7]. Furthermore, in permanent implants despite being essentially passive and not harmful to the human body, release of toxic debris because of wear can occur and cause inflammation reactions [8].
A short history of the use of magnesium in osteosynthesis

The history of magnesium for applications in osteosynthesis dates back to the beginning of the 20th century. As early as in 1906 Lambotte applied Mg as a degradable implant material for the fixation of bone fractures [9]. He used pure Mg plates in combination with gold-coated steel nails for the fixation of a fractured lower leg. Due to galvanic corrosion, the Mg plate degraded fast – it dissolved within only 8 days – and a large amount of gas was observed beneath the skin. However, he concluded that Mg is resorbable in the body. Despite this set-back further research in this area was undertaken (even by Lambotte) in animals and humans using different alloys [2, 9-11]. In 1913, Hey Groves noted enhanced callus formation by the use of Mg as intramedullary peg, but also fast degradation and fracture of the pegs. Therefore, he thought magnesium unsuitable for fixation of ordinary fractures, but suggested its use for old un-united fractures [2]. In 1934 Verbrugge investigated a Mg-8Al alloy and noticed that degradation was slow and a new callus formed, that magnesium is completely resorbable, neither toxic nor irritant, that it has an anaesthetic effect and that the evolved hydrogen does not cause any harm [11]. Similar findings were also reported by McBride who worked with Mg-4Al-0.3Mn [10]. He suggested magnesium to be suitable in hard cortical bone and to restrict the use of Mg in oblique or condylar fractures only to fractures where little stress is placed on the implants. Despite these promising results only little further research was undertaken and it took more than 50 years, until the beginning of the 21st century, for new investigations into the use of Mg as a biomaterial to start, e.g. [3, 12-15]. However, in the last years, this field became a “booming” research topic. Various Mg alloys were screened for their possible use in degradable implants. Thereby, many studies focus on the degradation behaviour, in vitro [16-22] and in vivo [3, 23-25]. However, today, there are still no Mg-based implant materials for osteosynthesis available on the market. Thus, it is the aim of this work to develop a suitable Mg-based implant, which can be used in osteosynthesis.

As the corrosion behaviour of Mg is important, when considering it for a degradable implant, section 1.2 will give a more detailed description of the corrosion of Mg and its alloys, as well as the biodegradation performance and its improvement.
1.2 Corrosion mechanisms of Mg and its alloys

Magnesium and its alloys show generally a rather low corrosion resistance in aqueous solutions [26, 27]. This limits its use in engineering applications, and surface coatings for protection might be required for a safe use [28]. However, for applications as a biodegradable material this is a key aspect. Corrosion of magnesium in aqueous solutions proceeds according to the following reactions (Eq. 1.1–1.4) leading to the formation of gaseous hydrogen and magnesium hydroxide [26, 27]. The magnesium hydroxide produced is (quasi-) passive and provides some protection to the bulk [27].

\[
\begin{align*}
\text{Mg (s) + 2 H}_2\text{O (aq)} & \rightarrow \text{Mg(OH)}_2 (s) + \text{H}_2 (g) \quad \text{(overall reaction)} \quad (1.1) \\
\text{Mg} & \rightarrow \text{Mg}^{2+} + 2 \text{e}^- \quad \text{(anodic reaction)} \quad (1.2) \\
2 \text{H}_2\text{O} + 2 \text{e}^- & \rightarrow \text{H}_2 + 2 \text{OH}^- \quad \text{(cathodic reaction)} \quad (1.3) \\
\text{Mg}^{2+} + 2 \text{OH}^- & \rightarrow \text{Mg(OH)}_2 \quad \text{(product formation)} \quad (1.4)
\end{align*}
\]

The corrosion performance of magnesium in aqueous solutions is pH-dependent; while Mg dissolves below a pH value of approximately 11.5 (depending on the ion concentration), it forms a passive Mg(OH)$_2$ film at higher pH values, as shown in the Pourbaix diagram (Fig. 1.2.1), where the dependence of the potential on pH is plotted [29]. Consequently, at the pH of blood (~7.3–7.4) Mg is actively dissolved.

Magnesium has a very low standard electrode potential; with a value of -2.37 V (vs. SHE) with respect to the hydrogen electrode potential taken as zero and at 25°C it is less noble than most metals and renders the Mg matrix anodic [27]. This leads to a high susceptibility of Mg and its alloys to galvanic corrosion and is a serious matter in Mg technology, as will be explained in the next section.
In the context of Mg alloy development for implant application in osteosynthesis, various corrosion mechanisms have to be considered. They are presented in the following sections.

**Galvanic corrosion**

Galvanic corrosion is observed as severe corrosion of the Mg matrix close to cathodic areas. A distinction can be drawn between external and internal galvanic corrosion depending on whether the Mg is in contact with a nobler metal or whether there exist cathodic second phases or impurities in the matrix. In the context of this study, internal galvanic corrosion is an important issue to be considered, as structural characteristics may bring about galvanic corrosion.

In pure magnesium, the impurity elements Fe, Ni or Cu play a considerable role; they have a detrimental effect on the corrosion performance of Mg even when present in only small amounts [30]. Due to their low solubility in Mg and low hydrogen overvoltage, they can form micro-galvanic cells and cause internal galvanic corrosion. Thus, during alloy production it is important to use high purity material to keep the impurity level below the tolerance limit. In Mg alloys the secondary phases present can
also act as (micro-) cathodes leading to dissolution of the Mg matrix adjacent to them. However, most alloying elements are less damaging than the impurity elements due to their higher hydrogen overvoltage and thus lower potential difference between anodic and cathodic regions in the alloy. Thus, regarding the electrochemical properties, the best candidate for a biodegradable implant would be high purity Mg. This, however, does not meet the mechanical requirements and is an undesirable approach.

Grain boundaries also represent cathodic regions to the anodic grain interior. Therefore, corrosion does not propagate along the grain boundaries, but takes place in the matrix close to the grain boundaries and eventually leads to undercutting and grain fallout [27]. However, in literature the role of grain size on the corrosion rate is controversially discussed [31-34]. Some report a fine microstructure to have more grain boundaries, which can act as corrosion barriers and increase the corrosion resistance [31-33]. But, it is important to consider the processing route [32, 33] because microstructural changes, such as the phase distribution or dislocation density, also affect the degradation behaviour. Dislocations, for example, are said to locally decrease the equilibrium potential and lead to accelerated dissolution [35]. Kutsniy et al., on the other hand, observed an increase in corrosion rate of fine-grained equal channel angular pressed (ECAP) samples compared to extruded samples and attributed it to the larger area of grain and interphase boundaries [34]. However, he did not consider microstructural changes (e.g. the dislocation density) by the different processing routes.

**Stress corrosion and stress corrosion cracking**

As a Mg implant used in osteosynthesis may be under load, corrosion under stress needs to be considered. In certain environments, Mg alloys can be susceptible to stress corrosion cracking (SCC) leading to sudden and unexpected failure of the sample. Al- and Zn-containing alloys show a high susceptibility to SCC, while pure Mg is not susceptible to SCC in atmospheric and most aqueous environments, but is in severe laboratory conditions (e.g. [36]). Zr- and rare earth-containing Mg alloys were reported to have an intermediate SCC susceptibility.
In literature, intergranular as well as transgranular SCC propagation was observed depending on the environment, the composition and the microstructure of the Mg alloys [36]. Intergranular failure is a continuous, entirely electrochemical process, where anodic dissolution of the matrix close to the grain boundaries occurs and the stress applied pulls the metal apart [36, 37]. Transgranular SCC was found as the main fracture mode in Mg alloys, two mechanisms are responsible for its occurrence [36]: crack propagation by dissolution including preferential attack or film rupture, and crack propagation by brittle fracture including cleavage or hydrogen embrittlement. Preferential attack of areas close to cathodic precipitates and stress concentrations increase local corrosion rates and accelerate dissolution [36]. In the film rupture model, the protective surface film is partially broken by local plastic deformation producing an electrochemical potential between the film and the film-free areas. In many studies, however, fracture surfaces were observed which contained striations, shallow surface steps and interlocking facets, which do not support the dissolution, but brittle fracture models [38]. Pardue et al. suggested a discontinuous process, where alternating mechanical and electrochemical stages are involved [37]. Pits and notches formed due to electrochemical attack lead to brittle fracture for a finite distance once high stress concentrations are reached. The crack stops at obstructions such as grain boundaries and proceeds once the obstruction is removed by electrochemical attack [37]. In Pugh’s brittle-film model a brittle film, e.g. an oxide, forms during slow corrosion, which is fractured in the following fast mechanical stage [38]. Once the crack has passed the brittle region, it is blunted by the ductile material, but can propagate if a new region gets embrittled, e.g. by re-formation of the surface film. Fairman et al. proposed that dislocation movement leads to rupture of the Mg(OH)₂ film by attack of the dislocations leading to the formation of corrosion tunnels, which fracture due to stress [39]. Hydrogen embrittlement (HE) was also reported to be responsible for SCC [36, 40]. However, the exact role of H is differently discussed. It was proposed that repeated H diffusion to the crack tip and formation of magnesium hydride can lead to brittle fracture or decohesion [41]. Other studies stated that atomic H in solid solution reduces the cleavage strength for transgranular and intergranular
fracture of the Mg matrix [42] or that H adsorption is responsible for HE by weakening the bonds at the crack tip [43].

### Biodegradation of magnesium and its improvement by surface treatments

The potential of Mg alloys for biodegradable implants has been widely recognised. In recent years various studies dealt with the biodegradation behaviour of different Mg alloys – mostly in vitro [12-22], but also in vivo [3, 23-25]. So far no standard procedure for evaluation of the biodegradation is available, however. Thus, in literature the biocorrosion behaviour was analysed by different techniques such as immersion testing and evaluation of the corrosion rate either by measuring the mass loss or the evolved hydrogen gas, by potentiodynamic and -static measurements or by electrochemical impedance spectroscopy. The tests were performed in various body-similar fluids, such as simulated body fluid (SBF), artificial plasma or Hank’s balanced salt solution, that reflect the ion composition and pH of human blood.

Rettig and Virtanen, for example, analysed the biodegradation rate of the Mg–Y–Nd alloy WE43 in SBF to be higher than in simple NaCl solutions [19]. Moreover, the corrosion product layer formed (inter alia amorphous phosphates) exhibited limited protective properties [19] and its composition depended on the elements present in the solution [20]. Moreover, the aggressiveness of Cl- ions was also observed in SBF [18]. In [18] an increased corrosion rate of pure and alkali-surface-treated Mg was found in normal SBF compared to SBF with reduced Cl- content. Other studies on the in vitro corrosion behaviour of various commercial Mg–Al–Zn alloys (AZ family) and pure (99.9%) Mg in Hank’s balanced salt solutions with and without Mg2+ and Ca2+ ions indicated that corrosion depends on the alloy and the test solution used [15]. The latter mainly influenced the composition of the corrosion product layer.

In first in vivo studies by Witte et al., four Mg alloys (two Al- and Zn-containing alloys AZ31 and AZ91 and two rare earth-containing alloys WE43 and LAE442) were implanted in the femur of guinea pigs. The in vivo corrosion rates of the alloys differed, LAE442 being reported to be the least active, and enhanced bone cell formation was found around the Mg implants compared to the reference implant made of polylactide
Moreover, in vitro corrosion proceeded faster than in vivo [3, 21]. In many studies Mg–Al–Zn alloys were investigated. However, aluminium should not be used for medical applications as it might have an influence on Alzheimer’s disease [44]. Thus, recent studies concentrate on Al-free, mostly newly developed alloys, such as Mg–Y–Zn [23], Mg–Ca [24, 45] or Mg–Mn–Zn alloys [25].

Generally, the optimum degradation performance of a bioabsorbable orthopaedic implant – initially slow and then increasing with time – can be achieved by surface modifications. Various technologies exist to produce surface coatings [28]. However, many of them provide permanent protection and are thus not suitable for degradable implants. And, only few surface treatments of Mg alloys for medical applications were reported in literature, e.g. [12, 15, 24, 46]. Chemical and/or thermal surface treatments such as heat treatments at elevated temperatures [15] or pre-immersion of pure Mg in an alkaline solution [12] were reported to increase the initial corrosion resistance. In [46], a fluoride treatment, where commercially pure Mg was immersed in 48% HF for 6–24 h, brought about significant improvement of the initial in vitro corrosion rate, but with time the coating became less effective [46]. In vivo tests of fluoride-coated Mg–Ca alloys indicated that such treated implants were clinically well tolerated, but did not lead to a significant improvement of the corrosion resistance [24]. Thus, to summarise, generally it is possible to tailor the degradation performance of Mg alloys by surface modification. Surface treatments, which result in the formation of a degradable coating, often bring about a reduction in the initial degradation rate, and lead to degradation of the substrate material after a certain time. However, the coating (and alloy) performance might differ in vitro and in vivo, thus once a suitable treatment is developed, its in vitro and in vivo performance must be analysed.

When planning to use a Mg alloy as a biodegradable implant material, not only the corrosion resistance needs to be considered but also the mechanical properties. Thus, high purity Mg which has a high corrosion resistance is not strong enough to meet the mechanical requirements. Similar is true for the often investigated cast alloys. In the following chapter attention will be paid to the mechanical properties of magnesium and its alloys.
1.3 Mechanical properties of Mg and its alloys

General aspects and influence of grain size on the mechanical properties

Due to their high specific strength, magnesium and its alloys are popular candidates for applications where weight-reduction and therefore energy-saving is required [1]. But, often the mechanical properties are insufficient, i.e. the absolute strength is rather low compared to other metals and the plastic deformability is limited due to magnesium’s hexagonal close-packed crystal structure, which exhibits only two independent slip systems (basal slip). Thus, the Taylor criterion, stating that five independent slip systems must be available for homogeneous plastic flow [47], is not fulfilled. However, at elevated temperatures, pyramidal and prismatic slip are activated and the ductility increases. Under ambient conditions, forming of magnesium alloys is difficult. Furthermore, due to the insufficient number of independent slip systems, preferential orientation of the crystals during forming occurs and thus a textured material is generated [48]. During extrusion, for example, the basal planes are mainly oriented parallel to the extrusion direction. Consequently, the mechanical properties of wrought magnesium are of a highly anisotropic nature. And, since the activation of deformation modes in magnesium depends on the direction of stress applied, i.e. twinning is more pronounced in compression than in tension [49], a tension-compression yield stress asymmetry due to twinning arises. However, an efficient way to overcome these issues and to significantly improve the strength and ductility of a Mg alloy is with a fine microstructure (of the castings and extrusions). Grain refinement during casting improves the chemical and structural homogeneity across the billet diameter. Moreover, the hot tearing susceptibility is reduced and extrusion facilitated. Furthermore, in a small-grained microstructure twinning is restricted due to geometric reasons.

A remarkable increase in tensile ductility in fine-grained pure magnesium having a grain size of 1–10 μm (Fig. 1.3.1a) was observed in 1962 by Chapman and Wilson [50]. In addition, a reduction of the “low-to-high-ductility” transition temperature by grain refinement was reported as seen in Figure 1.3.1b [50]. This significant increase in
room temperature tensile ductility by reducing the grain size cannot be explained by basal slip only; other deformation mechanisms are likely to be involved to induce such behaviour.

Koike and his team showed that in small-grained alloys, cross slip from basal to non-basal planes occurs easily; in grains of approximately 7 μm in size dislocations on basal and non-basal planes were present in the entire grain, while in 50 μm large (medium-sized) grains they were only observed in regions close to the grain boundaries [51-53]. Additionally, grain boundary sliding took place to some extent in the fine-grained material. Koike attributed this high dislocation activity to the grain-boundary compatibility stresses. As the compatibility stresses are localised to the region near the grain-boundary (a few μm) their effect is much higher in a material with small grains, where the influence extends over the entire grain volume [51-53].

Another effect of a small grain size is its improvement of yield strength through grain-boundary strengthening. This effect was found in the early 1950s by Hall and Petch [54, 55], who independently reported it. Thereby, the dislocation movement is blocked/pinned by the grain boundaries leading to a dislocation pile-up. As dislocations generate repulsive stress fields, which accumulate by piling up at the grain boundaries, dislocation sources in the neighbouring grain can be activated once the amount and stress field of piled up dislocations is large enough. Consequently, the material can be further deformed. Small grains, however, limit the amount of

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Figure 1.3.1: (a) Effect of grain size on the tensile ductility of pure Mg at room temperature and (b) “low-to-high-ductility” transition behaviour in dependence of temperature and grain size [50].
dislocation pile-up at the grain boundaries and thus higher stresses need to be applied to activate dislocations sources in the adjacent grain, leading to an increase in yield stress. The dependence of yield stress on grain size (Hall-Petch relation) is expressed in Eq. 1.5.

$$\sigma_Y = \sigma_0 + k_Y \cdot d^{-1/2}$$  \hspace{1cm} (1.5)

where $\sigma_Y$ is the yield stress, $\sigma_0$ the intrinsic yield stress, $k_Y$ the strengthening coefficient (also called the Hall-Petch slope) and $d$ the average grain diameter. $k_Y$ is said to be dependent on the critical resolved shear stress (CRSS) for the activated slip modes in the grains and on the misorientation of the neighbouring grains [56]. Because $\sigma_0$ and $k_Y$ depend on the active deformation mechanisms, i.e. slip and/or twinning, their values vary with the testing mode (tension or compression) [56-58], grain size [52], temperature [59] or presence of a deformation texture. Some values for $\sigma_0$ and for $k_Y$ found in literature are listed in Table 1.3.1.

Table 1.3.1: Various Hall-Petch parameters reported in literature.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Grain size control</th>
<th>Grain size (µm)</th>
<th>Testing</th>
<th>$\sigma_0$ (MPa)</th>
<th>$k_Y$ (MPa m$^{1/2}$)</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>pure cast Mg cast, grain-refined by Zr</td>
<td>36–1500</td>
<td>tension</td>
<td>17.7</td>
<td>0.25</td>
<td>0.39</td>
<td>[57]</td>
</tr>
<tr>
<td>Mg-2Zn cast, grain-refined by Zr</td>
<td>55–340</td>
<td>compression</td>
<td>3.1</td>
<td>0.47</td>
<td>0.54</td>
<td>[58]</td>
</tr>
<tr>
<td>AZ31 extruded and annealed</td>
<td>3–22</td>
<td>tension</td>
<td>17-30</td>
<td>20°C: 40</td>
<td>20°C: 0.30</td>
<td>[59]</td>
</tr>
<tr>
<td>AZ31 rolled and annealed</td>
<td>3–8.5</td>
<td>compression</td>
<td>20°C: 21•</td>
<td>200°C: 86*</td>
<td>200°C: 0.27</td>
<td>[59]</td>
</tr>
<tr>
<td>ZM21</td>
<td>7–25</td>
<td>tens./compr.</td>
<td>154/31</td>
<td>0.08/0.32</td>
<td></td>
<td>[56]</td>
</tr>
<tr>
<td>ZK30, ZE10, ZEK100 hydrostatic procedure</td>
<td>3–20</td>
<td>tens./compr.</td>
<td>200/100</td>
<td>0.21/0.49</td>
<td></td>
<td>[56]</td>
</tr>
</tbody>
</table>

* twinning-dominated flow  * slip-dominated flow

Grain refinement has the most pronounced effect on strengthening of Mg alloys. However, work hardening, solid solution strengthening and precipitation hardening are also possible strengthening mechanisms [60]. In work hardening the dislocation
density is increased by the forming process. Because of their repulsive and attractive stress fields, the dislocations interact with each other, which can lead to entanglement, which impedes dislocation propagation via pinning and thus increases the strength. The improvement of yield strength is described in Eq. 1.6, where $G$ is the shear modulus, $b$ the magnitude of the Burgers vector and $\rho_\perp$ the dislocation density.

$$\Delta \sigma_Y \propto G \cdot b \cdot \rho_\perp^{1/2}$$  \hspace{1cm} (1.6)

In solid solution strengthening, dislocation movement is hindered by lattice distortions – such as interstitial and substitutional point defects caused by the addition of the solute element – by interaction of the stress fields around solutes with those of the dislocations. The shear stress $\Delta \tau$ needed to move dislocations in a material is related to the increase in yield stress and depends on the solute concentration $\varepsilon$ and the lattice strain $\varepsilon$ due to the solute, the shear modulus $G$ and the magnitude of the Burgers vector $b$ (Eq. 1.7).

$$\Delta \tau \propto G \cdot b \cdot \varepsilon^{1/2} \cdot \varepsilon^{3/2}$$  \hspace{1cm} (1.7)

When alloying with an element above its solubility limit, precipitation hardening can occur generating particles of a second phase. Thereby, the second-phase particles generate stress fields, which can interact with those of the dislocations. Dislocations can either cut through these particles when they are small ($r \sim 5 \text{ nm}$) (Eq. 1.8) or bow around them when they are larger ($r \sim 30 \text{ nm}$) (Eq. 1.9) resulting in longer dislocations and an increase in yield stress.

Particle cutting: \( \Delta \sigma_Y = \Delta \gamma_S \cdot \pi \cdot r \cdot (b \cdot L)^{-1} \)  \hspace{1cm} (1.8)

Particle bowing: \( \Delta \sigma_Y = G \cdot b \cdot (L - 2r)^{-1} \)  \hspace{1cm} (1.9)

where $\Delta \sigma_Y$ is the increase in strength by particle cutting or bowing, respectively, $\Delta \gamma_S$ is the increase in surface energy by cutting of the particles, $r$ the radius of the particle, $b$ the magnitude of the Burgers vector and $L$ the spacing between the pinning points.
To optimally exploit precipitation strengthening, several Mg alloys can be age hardened, although the age hardening response is not as pronounced as for example in some Al alloys and depends on the alloy composition [61]. Strengthening phases precipitate in the shape of plates or rods parallel to the \( \langle 0001 \rangle_a \) direction and lie along the \( \{10\overline{1}0\}_a \) and \( \{11\overline{2}0\}_a \) planes [61]. Nie calculated the plate-shaped precipitates formed on prismatic planes to be the most effective dispersion strengtheners under identical volume fractions and number densities of precipitates per unit volume [62]. Moreover, a high number density and/or a high aspect ratio of precipitates are also beneficial for strengthening [62].

**Grain refinement of magnesium**

To summarise, grain refinement is an efficient method to improve the chemical homogeneity, the formability and the mechanical properties of Mg alloys. On the one hand a significant increase in ductility can be achieved due to the activation of different deformation modes, on the other hand the yield strength can be improved by grain-boundary strengthening. There exist different technological casting processes to achieve a fine microstructure as summarised in [63]. In many of them a grain-refining agent is added, as grain refinement was reported to mainly depend on the number of nucleants. StJohn et al. [63, 64], however, elaborated a model on grain refinement in Mg alloys based on a model on Al alloys of Easton and StJohn [65-67], where the potency of the nucleant particles and the segregating power of the solutes are important [63]. Thereby, the former is defined as the undercooling required for nucleation \( \Delta T_n \), and the latter as the growth restriction factor (GRF) \( Q \). The GRF is given in Eq. 1.10 and expresses the growth-restricting effect of solute elements on the solid-liquid interface of new grains as they grow into the melt. The addition of solutes generates constitutional undercooling ahead of the advancing solid-liquid interface. In the constitutionally undercooled zone, segregating elements slow the growth rate, thereby allowing more time for nucleation to occur and consequently restricting grain growth. And, even more importantly, nucleants are activated in the diffusion zone in front of the interface impeding the growth of a previous grain.
\[ Q = m_l \cdot C_0 \cdot (k - 1) \] 

(1.10)

where \( m_l \) is the slope of the liquidus line (usually approximated to a straight line), \( C_o \) the concentration of the alloy and \( k \) the partition coefficient (i.e. \( k = C_s / C_i \) at the interface temperature, where \( C_s \) and \( C_i \) are the concentrations of the solute in the solid and liquid phases, respectively).

To calculate the grain size of the castings, it is assumed that constitutional undercooling \( \Delta T_c \) is the dominant undercooling available and that a nucleation event begins when \( \Delta T_c \) reaches \( \Delta T_n \), the undercooling necessary for nucleation, due to growth of a previously nucleated grain. Then the grain size \( d \) can be estimated using Eq. 1.11.

\[
d = a + \frac{b}{Q} = \frac{a'}{\sqrt[3]{\rho \cdot f}} + \frac{b' \cdot \Delta T_n}{Q} 
\] 

(1.11)

where \( a \) is related to the number of active nucleants at infinite \( Q \) values, which are represented by their particle density \( \rho \) and their activated fraction \( f \), while \( b \) is related to the potency of the nucleant particle expressed by the constitutional undercooling required for nucleation \( \Delta T_n \).

Once fine-grained castings are available, the mechanical properties can be further improved by thermo-mechanical processing, which lead to a further decrease in grain size, as was performed in this study (i.e. extrusion). In order to maintain the mechanical properties, energy release during the forming process resulting in grain coarsening must be avoided. In addition, when the aim is fine-grained end products fine-grained castings are essential as grain boundaries and second phase particles may initiate recrystallisation [68]. Moreover, by the presence of fine second-phase particles, grain boundary movement can be prevented; small particles exert a pinning pressure, which counteracts the driving force of boundary motion. Grain boundary pinning is most effective when the number of particles is large and their size small.
1.4 Aims and outline of the thesis

In this project a Mg-based biodegradable implant material for osteosynthesis should be developed. Requirements of the material are high yield and fatigue strength, moderate ductility, slow degradation performance and biocompatibility. Thus, a combination of suitable mechanical, electrochemical and biological properties is required. In this work, two different approaches were elaborated. In the first part, a commercially available Mg–Y–RE alloy was investigated for its possible use. The focus lay on optimising the degradation behaviour, i.e. improving the initial degradation resistance by various surface treatments, and understanding the occurring corrosion mechanisms. In the second part, a novel Mg alloy system was developed on the basis of the grain refinement model of StJohn et al. [63, 65-67]. The efficiency of the approach is discussed and the positive influence of the alloy composition on the casting process (i.e. reduction of hot tearing) is explained by thermodynamic calculations. Moreover, the mechanical properties are systematically analysed and explained and the degradation performance of un-treated and surface-modified samples is evaluated.

Improvement of the initial degradation rate by surface modification

A promising material for implants in osteosynthesis is the Mg alloy WE43; it has considerable strength and corrosion resistance, and its alloying elements are assumed to be non-toxic. Its chemical composition according to ASTM designations is 3.7–4.3 wt.% Y, 2.4–4.4 wt.% rare earth elements (consisting of Nd and heavy RE such as Yb, Er, Dy or Gd), ~ 0.4 wt.% Zr and Mg as balance. However, tests in body similar fluids show that WE43 corrodes relatively fast at the beginning of immersion, until a protective layer of corrosion products has formed, which slows the degradation process. But, as corrosion of Mg is associated with the production of hydrogen gas and as at the beginning of implantation the tissue is injured and more sensitive, the initial corrosion rate should be reduced. Thus, Chapter 2 focuses on the improvement
of the initial degradation resistance of the commercial alloy WE43 by according surface treatments.

In Chapter 2.2 and 2.3 the influence of thermal treatments on surface oxide formation and degradation behaviour is explored. By this simple technique, a significant improvement of the initial corrosion rate is achieved. However, due to the ceramic character of the layer, it cracks when it is deformed and consequently partially loses its protective ability. Chapter 2.4 deals with a commercially produced ceramic coating and its influence on the degradation behaviour when exposed to load. To avoid loss of the coating’s protective function due to cracking, in Chapter 2.5 biodegradable metallic Zn coatings are electroplated for surface protection. The laboratory work concentrated on new chemical pre-treatments prior to electroplating, which are necessary in order to obtain good adhesion between the substrate and the Zn coating, and their understanding, but also on the degradation performance of such coated substrates.

**Designing new magnesium alloys**

To improve the mechanical and electrochemical properties compared to the commercial alloy WE43, new Mg alloys were developed. Due to the positive influence of a small grain size on the mechanical properties of Mg alloys, the alloy development aimed at a fine microstructure. For alloy development the grain refinement theory by StJohn et al. [63, 65-67], explained in 1.3, was taken as a basis for the choice of elements, which are mainly elements with high $Q$ values and which are tolerated by the body. Regarding the degradation performance, it was the aim to produce a nobler matrix by solid solution with a more corrosion resistant element. Moreover, the formed corrosion product layer shall have a high protective ability.

As during production of the alloys by vertical direct chill casting a remarkable decrease in hot tearing susceptibility was observed in the presence of the elements Yb and Y, further experiments and thermodynamic calculations were performed to understand this phenomenon, as described in Chapter 3.1. Chapter 3.2 focuses on the design strategy of the new alloys and its effect on the microstructure and the
mechanical properties of the new alloys, the degradation performance and its improvement by surface treatments.

1.5 References


Chapter 2

Surface modifications of magnesium alloys for tailoring degradation behaviour

2.1 Introduction

The generally low corrosion resistance of magnesium and its alloys is a key factor for its potential use as biodegradable implant material. However, often the initial degradation proceeds quickly, leading to a local pH increase and enhanced hydrogen gas production shortly after implantation, which might further irritate the already injured tissue. Additionally, early loss of implant stability may occur before the tissue has sufficiently healed for load carrying. A simple way to improve the degradation performance is by surface modification; the contact between the Mg substrate and the environment is prevented and corrosion inhibited or delayed. However, it should be considered that the coating must first provide protection of the implant (in the early stage after implantation) and later, with time and bone growth, it should also degrade. There exist different industrial coating techniques for Mg, such as conversion coating, anodising, vapour-phase deposition or electrochemical plating [1]. In addition, chemical, thermal and combined chemical and thermal surface treatments were reported in literature to improve the corrosion performance of Mg alloys [2-4]. However, in many coating processes, corrosion-resistant and thus permanent coatings are deposited, fulfilling the needs of permanent applications, e.g. in the transportation industry [1]. Moreover, often chemicals are used, which might be harmful to the
human body. Thus, coating processes for medical implants need to be chosen carefully. In this work, various surface treatments were evaluated, such as heat treatments, anodising, vapour-phase deposition or electrochemical plating, which aim at improving the initial degradation resistance of the Mg alloy and which should degrade with time. Conversion coating, where the surface is converted into a chromate, phosphate or other ceramic compound [5-10], was not considered because the layers produced tend to be inhomogeneous and may contain cracks as they form by nucleation and precipitation from a metal solution on the substrate [7].

The surface oxide layers formed by heat treatments at elevated temperature or by anodising are shown to be an effective way to protect the Mg substrate. But, due to the ceramic character of these films they are brittle and can crack during plastic deformation, which can occur during implantation. This can be overcome by a metallic coating, deposited either by electrochemical plating or by vapour deposition processes. The choice of possible metals, however, is limited because only biodegradable and biocompatible elements can be used. As most metals are nobler than Mg the coating must not only provide good adhesion to the substrate, it must also be homogeneous and pore-free to avoid galvanic corrosion. One possibility to avoid drastic galvanic corrosion is the deposition of high purity (HP) magnesium on a Mg alloy [11-13]; the corrosion resistance of HP Mg with low impurity content is high [14] while the electrode potential difference between substrate (i.e. the Mg alloy) and coating is small. In [11, 12] a simple vapour deposition process was described, where in a furnace with five heating zones, 3N grade Mg was evaporated and deposited on an AZ31 substrate, which was positioned at a lower temperature. In corrosion tests such coated samples performed comparably to 6N grade Mg due to the purifying effect of evaporation and corroded much less than un-coated AZ31 specimens. Inspired by these results, experiments using a similar set-up were performed in this study; a 3N grade Mg evaporation source and a Mg–Y–RE alloy (WE43) substrate were placed at different temperatures in a steel tube in a horizontal oven. Various temperature profiles and positions in the steel tube were investigated. It turned out that Mg deposition was successful and Mg crystals were detected for certain
deposition parameters. However, differently to reported elsewhere, only the substrate area facing the evaporation source was covered with magnesium, the quality of adhesion varied depending on the deposition parameters and the reproducibility of the experiments was poor. Therefore, this simple technique of vapour deposition had to be abandoned.

In the following, various surface modifications on the Mg–Y–Nd alloy WE43 (see also section 1.4) are described and discussed, focussing on the deposition process and the corrosion behaviour. Heat treatments at elevated temperatures (of around 500°C) are shown to be a simple method to remarkably improve the initial degradation performance compared to polished WE43 substrate by formation of a protective surface oxide layer. In the following, the oxide formation and corrosion mechanisms will be discussed in detail. Then, the degradation behaviour of plasma-electrolytic oxidation treated (Magoxid-Coat®) samples under tensile stress is investigated. Magoxid-Coat® is a porous ceramic Mg oxide coating produced by AHC Oberflächentechnik, Germany, in an anodising process with spark discharging [15]. It was considered as alternative to bare WE43 by the industry partner of this project as in preliminary in vitro and in vivo studies uncoated WE43 samples seemed to degrade too fast. In this study, the coating is characterised and its influence on the degradation performance under an applied tensile load investigated. Because the oxide layers are brittle and because during surgery of such-treated implants plastic deformation and thus cracking of the surface layer might occur, their protective influence is decreased. Thus, in another approach, a biodegradable metallic (and thus ductile) Zn coating was electrodeposited, which is expected to deform with the substrate without losing its protective function. Here, the focus lay on the development, characterisation and understanding of the deposition process consisting of a chemical pre-treatment, where a Zn underlayer is produced reducing the activity of the surface, and the electroplating itself. In the second part the protective ability is tested in simulated body fluid.
2.2 Influence of heat treatments on the biodegradation performance of a Mg–Y–RE alloy in simulated body fluid

Introduction

Thermal treatments are a simple and efficient tool to alter the microstructure and/or the surface state of alloys and improve thereby the corrosion resistance [3, 4, 16]. Davenport et al. showed by synchrotron X-ray microtomography that cast and heat-treated WE43 pins corroded slower than their as-cast counterparts due to homogenisation of the Y distribution [16]. In [4], an artificial corrosion–oxidation surface treatment, where the Mg alloy AZ31 was first chemically treated in an alkaline solution (pH 12) to form a magnesium hydroxide layer and then heat-treated at 400–500°C to transform it into magnesium oxide, was reported to retard filiform corrosion. Samples which were heat-treated only also exhibited an improved degradation resistance compared to polished specimens [4]. A similar study on a differently treated binary Mg–Ca alloy (alkaline immersion followed by a heat treatment) led to the same conclusions [17]. However, no comparison with only alkali-treated or only heat-treated specimens was undertaken with the Mg–Ca alloy. In binary Mg–Y alloys with varying Y content heat treatments at temperatures between 450 and 550°C indicated the formation of coexisting MgO and Y₂O₃ protective oxide upon heat treatment [18]. But, there the corrosion resistance was not investigated.

In this study on the one hand the analysis of the influence of different heat treatments on the initial degradation behaviour of WE43 and on the other hand the influence of surface state on the degradation performance is investigated. The Y-containing surface film formed by thermal oxidation treatments was studied in detail and its influence on the initial degradation rate in physiological media was evaluated.

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Experimental

Sample preparation and denotations

Discs of 22 mm in diameter and 3.6 mm in thickness were cut from an extruded WE43 bar. They were ground and polished (to 0.25 μm diamond polish) and ultrasonically cleaned. To examine the influence of the heat treatments on the surface film formation, the samples were polished before the oxidation heat treatment (oxidised series); for microstructure analysis and to obtain polished reference material, the samples were polished also after the heat treatment (polished series). The oxidation heat treatment was performed at 500°C for 1, 8, 24, 48 and 168 h (1 week) and followed by air-cooling leading to the formation of a surface oxide layer, which was not removed from the specimens. The samples were placed on a tripod made of alumina sticks in order to allow for a homogeneous oxidation. For the polished sample series, the material was first heat-treated at 525°C for 6 h and water-quenched (solution heat-treated condition, SHT) and then ground and polished. On some samples an additional artificial ageing treatment (16 h at 250°C) was done (T6 condition) before polishing. All heat treatments were performed in an air-circulating furnace. The sample denotations and series, which will be used throughout the following text, are listed in Table 2.2.1.

Table 2.2.1: Heat treatments, sample denotations and sample series.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Annealing time (h)</th>
<th>Label</th>
<th>Sample series</th>
</tr>
</thead>
<tbody>
<tr>
<td>525</td>
<td>6</td>
<td>SHT</td>
<td>p*</td>
</tr>
<tr>
<td>525 + 250</td>
<td>6 + 16</td>
<td>T6</td>
<td>p</td>
</tr>
<tr>
<td>500</td>
<td>1</td>
<td>ox1</td>
<td>ox**</td>
</tr>
<tr>
<td>500</td>
<td>8</td>
<td>ox8</td>
<td>ox</td>
</tr>
<tr>
<td>500</td>
<td>24</td>
<td>ox24</td>
<td>ox</td>
</tr>
<tr>
<td>500</td>
<td>48</td>
<td>ox48</td>
<td>ox</td>
</tr>
<tr>
<td>500</td>
<td>168</td>
<td>ox168</td>
<td>ox</td>
</tr>
</tbody>
</table>

* polished     ** oxidised

Microstructure and characterisation

The microstructures of all samples were analysed by optical microscopy. Isothermal thermogravimetric analysis (TGA) was performed (Netzsch STA 449C). In addition,
the oxidised specimens were investigated by X-ray diffraction (XRD) and Auger electron spectroscopy (AES). The TGA measurements were carried out at 500°C in air for 120 min and the mass gain over time was recorded. The samples measured 5 mm x 5 mm x 9 mm and were ground with emery paper up to grit 4000 and degreased in isopropanol directly before measurement. For phase identification of the oxidised samples XRD measurements (PANalytical X’Pert PRO-MPD) were conducted using a Cu Kα1 (λ = 0.15406 nm) source operated at 38 kV and 45 mA. AES (Perkin-Elmer PHI 4300 SAM) was performed at 5 keV using a LaB₆ filament. Depth profiles were recorded using an Ar ion gun operated at 4 keV. The sputter rate, calibrated for Ta₂O₅, was 25 nm min⁻¹. Due to a thicker surface oxide, the ox48 and ox168 samples’ sputter rate was increased to 37.5 nm min⁻¹ and 75 nm min⁻¹, respectively.

**Immersion testing**

The degradation performance was evaluated by immersing the samples in simulated body fluid (SBF). The so-called hydrogen evolution method developed by Song et al. [19] was used to measure the corrosion rate. By measuring the volume of hydrogen gas which evolves during corrosion of magnesium and which is proportional to the amount of dissolved magnesium, the degradation rate over time can be estimated. Thereby, the sample is placed in a beaker containing the immersion solution and a measuring cylinder filled with the liquid is placed over it to collect the hydrogen formed during corrosion of the sample. The SBF was prepared according to [20] with the ion concentrations as shown in Table 2.2.2. For the tests, 300 ml SBF per sample were used corresponding to 30 ml SBF per 1 cm² surface area. The temperature was kept constant at 37±2°C (in air in an incubator) and the starting pH was 7.35±0.05. The SBF was changed on a regular basis to avoid an increase in pH above a value of 8, to keep conditions as constant and body-like as possible.
Table 2.2.2: Ion concentrations (in mmol l⁻¹) of human blood and the SBF used [20].

<table>
<thead>
<tr>
<th>Ions</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Cl⁻</th>
<th>HCO₃⁻</th>
<th>HPO₄²⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blood*</td>
<td>142.0</td>
<td>3.6–5.5</td>
<td>1.0</td>
<td>2.1–2.6</td>
<td>95.0–107.0</td>
<td>27.0</td>
<td>0.65–1.45</td>
<td>1.0</td>
</tr>
<tr>
<td>SBF*</td>
<td>142.0</td>
<td>5.0</td>
<td>1.0</td>
<td>2.5</td>
<td>109.0</td>
<td>27.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

* pH: 7.3–7.4

Results

Microstructure

Slight differences in microstructural features were observed between the oxidised samples. The grain size reached approximately 100±50 μm after 1 h at 500°C and increased to values of 200–250 μm after longer annealing. Mainly Nd-rich particles were identified, indicating that a significant amount of Y was dissolved in the Mg matrix upon heat treatment [21]. There are also slight microstructural differences between the specimens of the polished sample series. While solution heat-treated samples exhibit microstructural features similar to those observed for the oxidised samples, T6 samples reveal Y-rich particles. Thus, in the latter a less homogeneous distribution and lower solid solution contents of Y can be assumed compared to SHT or oxidised specimens [22]. Their grain size, however, is similar to those of SHT specimens. In a recent study it has been shown that the grain size of a Mg alloy in the near-equilibrium state (wrought condition) does not significantly influence the degradation behaviour in a simulated body fluid [23]. Therefore the influence of the slightly varying grain size on the degradation performance of the samples investigated in this study is discounted.

Characterisation of oxidised samples

Isothermal TGA measurements at 500°C indicated that the mass gain due to oxidation approximately follows a square-root law over time. Very similar behaviour was also observed by Wang et al., who investigated the early oxidation behaviour of Mg–Y alloys at high temperatures [18]. XRD measurements, represented as normalised intensity over 2θ in Fig. 2.2.1, indicate Mg and Y₂O₃ as crystalline phases.
on the oxidised specimens. Intermetallic phases in the bulk or other oxide phases on the surface were either below the detection limit of the XRD device or did not occur in crystalline form. The intensity of the $Y_2O_3$ signal increases with increasing oxidation time, implying a growing oxide layer on the surface. AES depth profiles confirm the XRD and TGA findings (Fig. 2.2.2). In the polished state only a thin ($\approx 10$ nm) MgO layer is found on the surface, which grows naturally and is most likely rather amorphous. After thermal oxidation the surface layers consist mainly of O, Y and a little Mg. Other alloying elements (Nd, Zr and REs) were not detected in the oxide layer and are not displayed in Fig. 2.2.2. In contrast to the XRD measurements, AES depth profiles also display the presence of MgO, which is found mainly in the outermost part of the oxide layer (100–200 nm) but also to a marginal extent inside the oxide layer. However, the MgO contribution to the surface layer is minor. Further, it is emphasised that the oxide layer grows with increasing heat treatment duration. After 1 h at 500°C a layer thickness of approximately 500 nm is achieved. During further annealing at 500°C the layer grows to a thickness of approximately 800 nm after 8 h, 1200 nm after 24 h, 1900 nm after 48 h, and 2700 nm after 168 h. Again, a square-root law of oxide growth over oxidation time is seen, as already observed for
the initial oxidation during TGA measurements. Since the calibration for the thickness calculation from the sputter rate was conducted with Ta₂O₅ the absolute values given here may vary slightly due to different yields and sensitivity factors. However, this does not influence the general conclusion of a growing oxide layer, which exhibits square-root behaviour upon oxidation in air. In Fig. 2.2.2 it is important to pay attention to the Y content beneath the oxide layer. Even though the sensitivity of AES for low elemental amounts is limited, reduced Y content in the oxidised samples is recognisable, particularly for the ox1 samples.

![Figure 2.2.2: AES depth profiles of WE43 (a) in the polished state, and after oxidation in air at 500°C for (b) 1 h, (c) 8 h, (d) 24 h, (e) 48 h and (f) 168 h, respectively.](image)

**Immersion testing**

The degradation performance in SBF of the differently heat-treated samples is given in Fig. 2.2.3. One curve for each state represents the degradation behaviour of the three samples with the same heat treatment. Generally, the reproducibility of hydrogen evolution at a certain degradation time is moderate. This is mainly ascribed to the high reactivity of Mg in aqueous solutions in the neutral pH regime [24], which reduces the accurate predictability of corrosion attack. The relative errors of the data presented in Fig. 2.2.3 were less than 10%. To allow a clearer picture, however, error bars were not
included in the plot. Immersion testing in SBF revealed different trends for the two sample series. Annealed and polished samples (SHT, T6) feature a high initial degradation rate, which slows with time. The hydrogen evolution of these samples can be approximated by a parabolic law. The degradation can be characterised as rapid in the beginning (with an undesired initial “hydrogen burst”), but relatively homogeneous (Fig. 2.2.4a, b). The T6 samples even corroded slightly faster in the beginning than samples in the SHT state. After immersion the surface of the polished samples was evenly rough, with a deposition of corrosion products similar to those found in [25]. The degradation performance of the oxidised samples indicates certain differences between the briefly-oxidised samples compared to samples oxidised for a longer time, but essentially displays the same characteristics. Brief oxidation induces a low initial degradation rate, which at some point rapidly increases with increasing immersion time. The degradation becomes fast and rather inhomogeneous as soon as the protective oxide layer is penetrated or removed (Fig. 2.2.4c-e). Pronounced localised corrosion sites are observed in the areas of damaged oxide layer, where simultaneously the formation of corrosion products occurs. After a longer oxidation treatment a very slow and homogeneous initial degradation is observed. It remains slow as long as the oxide layer still covers a reasonable amount of the surface. Once the protective surface layer is penetrated or removed the degradation rate increases and sites of localised
corrosion grow but not as fast as observed in the briefly-oxidised samples (Fig. 2.2.4f-h). When larger areas of uncovered metallic substrate are exposed to the immersion liquid the degradation behaviour becomes similar to that of the briefly-oxidised samples. The degradation rate is nearly constant until the surface layer is removed and degradation is slowed. This takes longer than for the brief oxidation state, however, since the oxide layer is thicker.

It is important to note that once the oxide layer is almost completely removed the overall hydrogen evolution of the oxidised samples is larger than that of the polished counterparts.

![Figure 2.2.4: Photographs of immersed samples after different immersion periods in SBF at 37°C. (a) SHT, 1 day; (b) SHT, 7 days; (c) ox1, 1 day; (d) ox1, 7 days; (e) ox1, 11 days; (f) ox24, 1 day; (g) ox24, 7 days; (h) ox24, 11 days.](image)

**Discussion**

WE43 has been shown to be a suitable candidate for an implant application material [26-28]. This is essentially due to its excellent corrosion resistance in aqueous solutions, which allows relatively slow and homogeneous degradation. In addition, the good electrochemical properties are accompanied by considerable mechanical properties, which include an elastic modulus similar to that of human bone [27]. The good corrosion resistance of WE43 is ascribed mainly to the beneficial influence of
the alloying element Y. The incorporation of oxidised Y in the surface film was found to be the reason for the enhanced degradation resistance of Mg–Y alloys [29, 30]. In addition, Davenport et al. reported on the advantageous influence of Y-rich regions in the Mg matrix, which slow the propagation of corrosion [16]. They also showed that the corrosion resistance is enhanced by homogenising the distribution of Y (and of other alloying elements), which could be achieved by appropriate heat treatments.

We performed thermodynamic calculations to simulate the content of the alloying elements dissolved in the Mg matrix (α-phase) with respect to the temperature, using the Pandat software package [31]. The thermodynamic simulations were conducted assuming equilibrium states: they indicated the highest amounts of Y in solid solution for temperatures above 300°C. Below 300°C, the content of Y in the Mg matrix significantly decreases due to the formation of Y-containing precipitates [22]. According to the thermodynamic calculations, the consequences of the heat treatments performed in this study are as follows: (i) the highest amount of Y dissolved in the Mg matrix may be expected for the SHT and the oxidised samples; (ii) the T6 samples feature less Y in solid solution due to artificial ageing at 250°C after the heat treatment at 525°C.

Macroscopically the two sample series lead to two basically different types of degradation performance; these are schematically represented in Fig. 2.2.5a. Since degradation of such Mg samples is ascribed to a statistical process, H₂ evolution regimes rather than defined curves are used to qualify the degradation performance after a certain pre-treatment. The hydrogen evolution of the annealed and polished samples can be described by a parabolic law. The characteristics are a high initial degradation rate due to the large reactive metallic surface, which is initially exposed to the immersion medium (Fig. 2.2.5b). Over time the degradation slows due to the formation of corrosion products on the surface and their barrier action, which impedes further degradation as found also in [25]. Corrosion accompanied by surface layer formation due to deposition commonly follows a parabolic law over time since the reaction rate is controlled by the diffusion of reaction species through the surface layer [32]. The higher initial degradation rate of the T6 samples compared to the SHT
samples is ascribed to microstructural differences. Since the artificial ageing part of the T6 heat treatment enhances the formation of Y-containing precipitates the solid solution content of Y in the Mg matrix, and thereby its protective influence on degradation resistance, is diminished. The more heterogeneous distribution of Y, in turn, may lead to the formation of local cells. The second phase particles act as cathodes and induce the active dissolution of the Mg matrix. Since the SHT samples also lack a single-phase structure, this phenomenon also takes place here, though it is less pronounced than observed for the T6 samples.

![Graph](image)

Figure 2.2.5: (a) Schematic degradation performances of WE43 samples after different heat treatments; (b) initial surface condition of annealed and polished samples featuring a large reactive surface; (c) initial surface condition of oxidised samples carrying an oxide layer; (d) penetrated oxide layer upon degradation. \( X \) represents the reactive area fraction.

The degradation performance of the oxidised samples can first be approximated by a sigmoidal law. Initially, a very low degradation rate is observed due to the protective influence of the oxide layer, which covers the whole surface of the samples (Fig. 2.2.5c). As soon as the oxide layer is penetrated, however, the reactive surface area is increased (Fig. 2.2.5d) and degradation accelerates. With time the degradation is impeded at these sites due to the barrier action of deposited corrosion products, while at the same time at other sites “fresh” reactive surface is exposed to the liquid featuring accelerated degradation. This condition persists until most of the oxide layer is removed and corrosion products cover the degraded surface. Now degradation slows, similar to the annealed-polished samples, and tends towards parabolic
behaviour. The oxidation duration causes a delay in the onset of accelerated degradation with increasing oxidation time, plus a later turn-in to the parabolic behaviour, but does not change the basic type of degradation performance. The H₂ evolution regimes are also assumed to become broader with increasing oxidation time, due to the statistical process of the degradation (Fig. 2.2.5a). A thick oxide layer is assumed to contain more inhomogeneities than a thin layer because of the increasing influence of the difference in thermal expansion coefficients between the oxide and the metal. This in turn renders just when and where the first penetration of the surface layer will occur more unpredictable which finally generates the onset of increased degradation.

In Fig. 2.2.6a the development of the H₂ evolution curve shape of oxidised samples is illustrated. Once the oxide layer has been removed the oxidised samples basically degrade locally via the same mechanism as observed for the annealed and polished samples. Therefore one curve represents the annealed and polished condition indicated with a delayed onset, which is ascribed to the protection by the oxide layer at the beginning of immersion. Upon penetration of the surface layer the actual reactive surface area increases, and is denoted by the reactive area fraction Xᵣ. The reactive area fraction also significantly influences the curve development of the oxidised samples’ hydrogen evolution. Xᵣ follows a characteristic S-shaped curve from 0 to 1 and can be determined by evaluating the immersed samples after various immersion periods. The H₂ evolution curve shape of the oxidised samples is then the result of multiplying the annealed-polished curve shape by the Xᵣ curve. It is characterised by a steep increase at the beginning when the reactive area fraction is still increasing considerably. Later the degradation mechanism of the annealed-polished samples becomes more pronounced and mainly determines the curve evolution. Figure 2.2.6b presents the maximal H₂ evolution rate per reactive surface area for SHT, ox1 and ox24 samples. The error bars indicate the scattering of the three samples per condition. In the SHT samples the maximal degradation rate is observed at the beginning of immersion when the reactive surface area is maximal. The slope of the curve indicates the degradation rate. The reactive surface area of the oxidised samples was determined by evaluating
photographs of the immersed samples taken during every SBF change (i.e. at least every second day).

![Figure 2.2.6](image)

**Figure 2.2.6:** (a) Development of hydrogen evolution curve shape of oxidised samples; (b) maximal H$_2$ evolution rate per reactive surface area of SHT, ox1 and ox24 samples.

The reactive surface was identified as the areas where the oxide layer was removed or obviously damaged. Hence the maximal degradation rate per reactive surface area of the oxidised samples is found at the onset of the accelerated degradation regime where the H$_2$ evolution is increasing but only a very small reactive surface area exists. The onset was determined as the intersection of the tangents to the H$_2$ evolution curves of the initial and the increased degradation regimes, respectively. The indication is that the maximal H$_2$ evolution rate per reactive surface area is similar for the SHT and ox24 samples but significantly higher for the ox1 samples. Taking into account the small reactive surface area at the beginning of the increased degradation regime, the amount of H$_2$ evolved from the ox1 samples is astonishingly large. This phenomenon is emphasised when the H$_2$ evolution in the onset region of the ox1 and the ox24 samples is observed in more detail (see small inserts in Fig. 2.2.3.). Compared to the ox24 samples, the ox1 samples evolve much more H$_2$ within the same immersion period. The explanation for this phenomenon will be based on a depletion hypothesis.

Figure 2.2.7a schematically presents the Mg surface with oxide layer in air. The Y concentration in solid solution is given as a function of distance from the surface. In the bulk the Y concentration $C_0$ is defined. Directly underneath the oxide layer a
reduced Y concentration \( C_d \) is assumed, and will be discussed later. Ion currents and diffusion coefficients of the oxide and the metal are indicated in Fig. 2.2.7b. Since very little data is available on diffusion coefficients or activation energies of Y in Mg, or \( Y^{3+} \) and \( O^{2-} \) in \( Y_2O_3 \), the following assumptions have been made: (i) diffusion is hindered more in ionic materials than in metals due to the lower mobility and defect density at temperatures around 500°C; (ii) for the continuous formation of \( Y_2O_3 \), \( O^{2-} \) diffuses through the (already formed) oxide layer to the metal-oxide interface rather than \( Y^{3+} \) diffusing to the surface in contact with air. The latter assumption does not influence the general conclusion of the depletion hypothesis but arranges the effect more clearly. It follows that at the beginning of the oxide formation the diffusion of Y in the metal is rate-determining, while upon further oxidation the diffusion of \( O^{2-} \) through the oxide layer becomes the rate-determining process. This seems reasonable as diffusion of ion species in oxides is commonly determined by rather high activation energies and low diffusion coefficients, especially at the low homologous temperatures used in this study. Since the formation enthalpy of \( Y_2O_3 \) is approximately three times higher than that of MgO, a much higher oxygen affinity of Y compared to Mg results [33, 34]. Hence, Y will readily diffuse towards the alloy’s surface to form \( Y_2O_3 \), leaving behind a Y-depleted zone in surface-near regions (see \( \Delta c \) in Fig. 2.2.7a).
For the formation of an Y$_2$O$_3$ layer on the surface the following simplified condition must be fulfilled:

$$3 J^o = 2 J^y$$

(2.1)

where $J^o$ and $J^y$ are the diffusion currents of O$^{2-}$ in Y$_2$O$_3$ and of Y in Mg, respectively. According to Fig. 2.2.7b the diffusion currents can also be expressed by the following equations according to Fick’s law:

$$J^o = D^o \cdot b \cdot \frac{d\mu}{dx} = D^o \cdot b \cdot \frac{\Delta \mu}{d}, \quad J^y = D^y \cdot \frac{d\epsilon}{dx} = D^y \cdot \frac{\Delta \epsilon}{\xi},$$

(2.2)

where $D^o$ and $D^y$ are the diffusion coefficients of O$^{2-}$ in Y$_2$O$_3$ and of Y in Mg, respectively, $b$ a dimensional constant, $\Delta \mu$ the chemical potential difference between inner and outer side of the oxide layer, $d$ the thickness of the oxide layer, $\Delta \epsilon$ the concentration difference near the surface and $\xi$ the depth of the concentration gradient. Substituting (2.2) in (2.1), it follows that

$$2D^y \cdot \frac{\Delta \epsilon}{\xi} = 3D^o \cdot b \cdot \frac{\Delta \mu}{d} \quad \text{or} \quad \frac{\Delta \epsilon}{\xi} = \text{Const.} \cdot \frac{1}{d}$$

(2.3)

Hence, brief oxidation of the samples generates a significant Y-depletion in surface-near regions due to the considerable mobility of Y in Mg and the still rather short diffusion paths of O$^{2-}$ through the oxide layer (Fig. 2.2.7d). The Y approaching the metal-oxide interface is rapidly consumed by the formation of the oxide layer: the concentration gradient increases ($\Delta \epsilon = C_0 - C_i$). Upon longer oxidation, however, the concentration gradient levels out ($\Delta \epsilon = C_0 - C_d$), since now the rate-determining influence of the O$^{2-}$ diffusion through the oxide becomes more dominant (Fig. 2.2.7e). The diffusion path lengths through the oxide layer increase, the O$^{2-}$ supply at the metal-oxide interface decreases and the concentration gradient is weakened due to the still-high mobility of Y in Mg. For brief oxidation $C_0$ is assumed to be lower than
observed for long oxidation due to less time for the Y-rich particles to dissolve [21] (not indicated in Fig. 2.2.7).

The AES results illustrated in Fig. 2.2.2 reveal a reduced Y content beneath the oxide layer and thus support the viability of the proposed depletion hypothesis. The consequence of the Y-depletion and depletion hypothesis on the degradation performance of the oxidised samples is evident. As soon as the protective oxide layer is removed, the reactive surface is exposed to the immersion liquid. In the case of brief oxidation the considerable Y-depletion of the surface-near regions and the amount of still undissolved Y-rich intermetallics even generate an enhancement of the surface reactivity, which is displayed in the faster acceleration of degradation in the briefly-oxidised samples (small inserts in Fig. 2.2.3). This effect is not as pronounced for the samples oxidised for a long time because they feature a less pronounced Y-depletion and a higher solid solution content of Y. Hence, the increase in degradation is slower and the turn-in to the high corrosion rate regime takes longer. However, due to the Y-depletion the overall hydrogen evolution of the oxidised samples is higher than that of the annealed and polished samples where possible depletion was removed by polishing the surface after heat treatment (Fig. 2.2.3). After very long oxidation there is only minimal Y-depletion underneath the oxide layer and the maximal H₂ evolution rate per reactive surface approaches the values found for the SHT samples (Fig. 2.2.6b).

Basically the surface reactivity discussed above also influences the development of the H₂ evolution curve-shape of oxidised samples. Due to the higher Y-depletion and amount of Y-rich intermetallics the surface reactivity of briefly-oxidised samples is higher than that of samples oxidised for a long time. This would imply a modification in Fig. 2.2.6a which generates a steeper ascent of H₂ evolution in the accelerated degradation regime of briefly-oxidised samples. This detail was not included in Fig. 2.2.6a, however, because it affects only a small part of the curve-shape and does not change the general degradation behaviour.

A simple calculation illustrates the depth of the depleted zone. In Y₂O₃ about 78 wt.% Y is present. Assuming a layer thickness of approximately 1 μm, a linear
concentration gradient as illustrated in Fig. 2.2.7a, and a depletion \((C_0 - C_d)\) of 2 wt.% Y the depth \(\xi\) is calculated to be approximately 80 \(\mu\)m.

It is worth mentioning that once the corrosion mode changes from homogeneous to heterogeneous degradation upon sample immersion, prediction of the degradation performance is no longer possible. Severe localised corrosion probably initiates at a certain point in immersion time on every specimen, particularly on the polished samples which offer a large reactive surface area. Then the degradation rate significantly increases and can no longer be approximated by a parabolic law. Optical inspection of the briefly-oxidised samples immersed for longer time periods disclosed sites of localised attacks, which to a certain extent also explain the large amount of \(H_2\) evolved during immersion. However, the proposed models allow a good prediction of the degradation performance of such or similarly-treated WE43 samples, or in general of comparable Mg–Y alloys, as long as there is a certain continuity and consistency in the degradation.

It is debatable whether the different modes of cooling following heat treatment (water quenching for the SHT and polished samples in contrast to air cooling of the oxidised samples) further influences the degradation behaviour of the two sample series. It is not expected, however, that a large difference in the concentration of Y dissolved in the Mg matrix will arise via this procedure, because Mg–Y–RE alloys are not particularly quench-sensitive [35]. For the oxidised samples air cooling was chosen in order to reduce the susceptibility to defect formation in the oxide layer due to the difference in the coefficient of thermal expansion between metal and oxide. Further, the difference in annealing temperature (525°C for polished samples, 500°C for oxidised samples) is not expected to substantially influence the results of this study. 525°C was chosen for annealing the polished samples as this temperature represents a standard for the heat treatment (especially T6) of WE43 [35]. For oxidation a more universal temperature was selected, one further from the solidus temperature of the various alloys that have also been investigated in the course of the studies.

It was initially speculated that the increase in the pH value to 8 upon sample degradation would reduce the corrosion tendency so much that self-passivation would
begin, decreasing corrosion rates with increasing immersion times as indicated by the parabolic behaviour of annealed-polished samples. This, however, was not so: samples immersed in a titrated solution with a constant pH value featured the same degradation behaviour as the samples investigated in this study. Due to the constantly lower pH value they only degraded a little faster but showed essentially the same performance (parabolic law) as described here.

Further discussion addresses the issue of whether an increased degradation resistance accompanies increasing oxidation duration. Immersion testing with samples oxidised for 1 week at 500°C indicated that these samples are more prone to degradation than those oxidised for 24 h or 48 h. Thicker oxide layers are assumed to be more susceptible to crack formation because the difference in thermal contraction upon cooling has more significant consequences. This implies that samples oxidised for a very long time carry more potential sites where corrosion can initiate, even if they now possess a more homogeneous distribution of Y in the Mg matrix and a thicker oxide layer, i.e. less depletion beneath the oxide layer. Hence, in general a decreased degradation resistance is expected after very long oxidation at high temperatures. This has not been taken into account in Fig. 2.2.5, however, since it is difficult to predict the onset of the increased degradation regime in such samples.

Thermal oxidation has proved to be an efficient and simple method for increasing the initial degradation resistance of WE43 samples in SBF. In the context of potential implant applications, however, possible plastic deformation during the surgical intervention also has to be taken into account. Deformation upon placement of the implant may harm the oxide layer and decrease its protective influence. This issue is addressed in chapter 2.3.

Similar thermal oxidation treatments at lower temperatures are also expected to improve the initial degradation resistance, without altering the microstructure to the same extent. Similar high protection by the oxide layer, however, cannot be expected because the layer will be less thick due to the restricted mobility of the diffusion species at lower temperatures. AES depth profiles on samples oxidised at 325°C and
425°C have indicated much thinner oxide layers than found for samples oxidised at 500°C. Alterations in density must also be taken into account.

The results of immersion testing emphasise that heat treatment followed by removal of the protective oxide layer is unsuitable for achieving a reduced initial degradation rate, as sought in this study. The presence of further second phase particles and the reduced protective influence of Y in solid solution in the Mg matrix are, in particular, believed to be the cause of the lower initial degradation resistance of T6 samples as compared to SHT samples. In contrast, oxidation of the samples generates reasonable improvement of the degradation resistance, especially at the crucial early stage of degradation when slow degradation is most important for implant applications.

**Conclusions**

The degradation performance of WE43 in SBF after different types of heat treatment was investigated and the potential of these heat treatments for enhancing the initial corrosion resistance was analysed. Annealing followed by polishing and thereby removing the surface’s thermally-formed oxide layer turned out to be an unsuitable approach, because the samples in question suffer an increased initial degradation rate. The corrosion performance of annealed and polished WE43 exhibits parabolic behaviour, with decreased degradation over time due to the barrier action of corrosion products deposited at the surface. Samples left in the thermally-oxidised state, however, feature enhanced corrosion resistance at the beginning of immersion. The XRD, TGA and AES measurements indicated the presence of MgO and crystalline Y₂O₃ in the surface film, which grows with increasing oxidation duration. The decreased initial degradation rate of oxidised WE43 is ascribed to the protective effect of this oxide layer. Once the layer is penetrated or removed, degradation accelerates until the deposition of corrosion products slows further degradation. Thermal oxidation proved to be a simple method for increasing the initial degradation resistance of WE43 in SBF. The varying degradation performance of the variously
treated samples is connected with the different surface states and is explained on the basis of a depletion hypothesis. Solution heat-treated WE43 contains a relatively high amount of dissolved Y in the Mg matrix whose beneficial influence on degradation resistance is mirrored in comparably low maximal degradation rates. In contrast, brief oxidation generates reasonable Y-depletion underneath the oxide layer, which causes significant acceleration of degradation once the surface film has been removed. The diminished beneficial influence of Y in the Mg matrix is identified as the cause of this. Long oxidation results in less Y-depletion, and the samples involved exhibit a maximal degradation rate similar to that observed in the annealed-polished samples. The models proposed here allow a good prediction of the degradation performance of such or similarly-treated WE43 samples, or in general of comparable Mg–Y alloys, as long as there is a certain continuity and consistency in the degradation.
2.3 Influence of heat treatment and plastic deformation on the biodegradation of a Mg–Y–RE alloy

Introduction

This chapter also deals with surface-oxidised WE43 specimens. However, the focus lies on the influence of plastic deformation on the degradation behaviour, which might occur during implantation and which could reduce the protective ability of the surface oxide. Thereby, the biodegradation behaviour of extruded WE43 in various heat treatment states was analysed by means of electrochemical impedance spectroscopy (EIS). The heat treatments were performed to change the bulk properties of the material, such as the distribution of Y, as well as to form a protective oxide layer on the sample’s surface. To check the bulk properties “polished” samples were tested in the T5 state (extruded and artificially aged), the solution heat-treated state, and the T6 state (solution heat-treated and artificially aged). For examination of the influence of the oxide layer on the degradation process, solution heat-treated and T6 states were chosen. Here the oxide layer formed during the heat treatment was left on the sample surface. Any oxide layer, naturally formed or grown by heat treatments, is rather brittle compared to the underlying metal and therefore prone to rupture when the material is strained, as could happen during the implantation process. Therefore the electrochemical response of cracked surface oxide layers, produced by straining of the samples, was also studied. All tests were carried out in two relevant body-similar solutions.

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**Experimental**

**Sample material and preparation**

The magnesium alloy investigated was an extruded WE43 bar of 25 mm in diameter. After extrusion all the material was aged for 16 h at 250°C, resulting in precipitation of Y-containing intermetallic hardening phase (T5 state).

For EIS, discs of 1.8 mm in thickness and 25 mm in diameter were cut perpendicular to the extrusion direction (transversal cross-section). All samples were ground using abrasive paper of grit 1200, 2400 and 4000 and water as coolant and then polished using diamond paste with a particle size of 3 and 0.25 μm, respectively, and isopropanol as lubricant. After the grinding and after each polishing step the samples were ultrasonically cleaned in isopropanol and dried in hot air.

In order to bring Y into supersaturated solid solution, the material was solution heat-treated for 5 h at 525°C and water-quenched (SHT). To gain high strength and hardness by precipitation hardening, the SHT-material was additionally aged for 16 h at 250°C and cooled in air (T6 state). All heat treatments were carried out in an air-circulating oven (Heraeus 750/2). The heat treatment at 525°C not only changes the microstructure of the material, but also generates a thermal oxide layer on the metal surface. To investigate the influence of the heat treatment on the bulk material, the samples were polished after the heat treatments described above.

In addition, flat bar tension specimens were machined parallel to the extrusion direction (longitudinal cross-section), ground and polished as described above and then solution heat-treated. Subsequently, the samples were strained to 5 and 9%, which is close to uniform strain, with an initial strain rate of 10^{-3} s^{-1}. Shortly after straining, the EIS measurements were carried out. Evaluation of the surface topography was performed on the differently-strained samples before EIS using scanning electron microscopy (SEM, LEO Gemini 1530 FEG-SEM). The acceleration voltage was 5 kV and the working distance (WD) approximately 10 mm.
Characterisation

The microstructures of the samples were analysed by optical microscopy (OM), SEM (CamScan) and energy dispersive X-ray spectroscopy (EDX, NORAN Instruments). Auger electron spectroscopy (AES) of the polished and oxidised samples was carried out on a Perkin-Elmer PHI 4300 SAM. Depth profiles were performed using an Ar ion gun, operated at a voltage of 4 keV and leading to a sputter rate of approximately 25 nm min\(^{-1}\); acquisition of the AES spectra took place after each sputter cycle.

The EIS measurements were performed on an Autolab PGSTATS 302 device equipped with a frequency response analyser (FRA). The measured frequencies ranged between 10\(^5\) and 10\(^{-2}\) Hz in the single sine AC acquisition mode with applied amplitude of 10 mV. A common three-electrode setup was used, the reference electrode being a saturated calomel electrode (KCl/Hg₂Cl₂), the counter electrode a cylindrical platinum grid and the working electrode the sample investigated. The measurements were performed at open circuit potential (OCP) with an equilibrium time to receive OCP of 5 minutes. Before measurement the sample surface was reduced to an area of 1 cm\(^2\); the rest was sealed with silicon (Dow Corning 732) and then dried. As electrolytes, two body-similar fluids were used: simulated body fluid (SBF), SBF27 in [20], and artificial plasma (AP) [36]. The pH value of SBF (buffered solution) was adjusted with concentrated hydrochloric acid to 7.4 at room temperature, while that of AP (non-buffered solution) was around 8. The composition of both solutions as well as that of blood is listed in Table 2.3.1.

<table>
<thead>
<tr>
<th>Ions</th>
<th>Na(^+)</th>
<th>K(^+)</th>
<th>Mg(^{2+})</th>
<th>Ca(^{2+})</th>
<th>Cl(^-)</th>
<th>HCO(_3^-)</th>
<th>HPO(_4^{2-})</th>
<th>SO(_4^{2-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blood*</td>
<td>142.0</td>
<td>3.6–5.5</td>
<td>1.0</td>
<td>2.1–2.6</td>
<td>95.0–107.0</td>
<td>27.0</td>
<td>0.65–1.45</td>
<td>1.0</td>
</tr>
<tr>
<td>SBF27*</td>
<td>142.0</td>
<td>5.0</td>
<td>1.0</td>
<td>2.5</td>
<td>109.0</td>
<td>27.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>AP**</td>
<td>144.5</td>
<td>5.4</td>
<td>0.8</td>
<td>1.8</td>
<td>125.3</td>
<td>26.2</td>
<td>3.0</td>
<td>0.8</td>
</tr>
</tbody>
</table>

* pH: 7.3–7.4  ** pH: 8.0

The SBF was used as it has nearly blood-like ion composition, while AP is according to ISO standard for medical device testing [36]. For comparison, additional...
measurements in a standard corrosion solution, a 3.5 wt.% NaCl solution with a pH value of 6, were carried out. To exclude a noticeable change in the electrolyte composition and pH due to dissolution of the sample and thus formation of hydroxide ions during the measurement, a large amount of electrolyte (900 ml cm⁻²) was used. Measurements of the pH before and after the test revealed no change.

The influence of time on degradation behaviour was investigated by 24 h measurements, where impedance data over the duration of 24 h was collected (measured every 2 h). All tests were carried out at room temperature; per measurement series at least two samples were examined. An overview of all samples investigated is given in Table 2.3.2. After EIS cross-sections of the samples were embedded and analysed by SEM and EDX to evaluate the microscopic corrosion behaviour.

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>Surface condition</th>
<th>Testing solutions</th>
<th>Additional tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>T5 (16 h at 250°C)</td>
<td>polished</td>
<td>SBF, AP, NaCl</td>
<td>longitudinal sample in AP</td>
</tr>
<tr>
<td>SHT (5 h at 525°C)</td>
<td>polished</td>
<td>SBF, AP</td>
<td>24 h measurement in SBF</td>
</tr>
<tr>
<td>T6 (SHT + T5)</td>
<td>polished</td>
<td>SBF, AP</td>
<td>24 h measurement in SBF</td>
</tr>
<tr>
<td>SHT, strained (to 5 and 9%)</td>
<td>polished</td>
<td>SBF, AP</td>
<td>longitudinal sample (0%) in AP</td>
</tr>
</tbody>
</table>

**Results**

**Unstrained samples**

The optical micrographs of samples in the T5 state revealed an average grain size of 15±5 μm (Fig. 2.3.1a, b). Two kinds of precipitates were observed: big, bright precipitates of 1–5 μm in size predominantly found at grain boundaries (indicated with arrows) and dark constituents, aligned in extrusion direction, with sizes smaller than 3 μm. Due to this alignment the latter were assumed to have formed directly from the melt and were already present during extrusion. The EDX and SEM analysis revealed that the big, bright precipitates are rich in Nd. Among the aligned constituents two
different phases were detected: large constituents approximately 3 μm in size and rich in Nd and smaller ones (around 1 μm) rich in Y.

During the solution heat treatment, the grains grew to approximately 50–200 μm; the bright precipitates were largely dissolved by the heat treatment; thereby their grain boundary pinning effect was reduced and thus grain growth occurred, while the big dark constituents mainly remained (Fig. 2.3.1c, d). However, care needs to be taken when comparing the micrographs of the differently heat-treated samples, because the SHT samples had to be etched for longer to render the microstructure visible and therefore etching artefacts might cause the precipitates to appear in a different way. The microstructure of T6 samples resembled the SHT state. Optically, no visible changes in the microstructure could be found: the Y-rich hardening precipitates formed during ageing at 250°C were too small to be detected by optical microscopy.

![Microstructure images](image-url)

**Figure 2.3.1:** Microstructure of various heat-treated samples; (a) T5, transversal cross-section; (b) T5, longitudinal cross-section; (c) SHT, transversal cross-section; (d) SHT, longitudinal cross-section. Arrows indicate Nd-rich precipitates along the grain boundaries.

To compare the degradation behaviour of the various samples the polarisation resistance (R_p), which is approached by the impedance values at low frequencies and
which is inversely proportional to the corrosion current, needs to be taken into account. To approximate a simple equivalent circuit consisting of a resistor $R_c$ in series with a combination of a resistor $R_p$ – capacitor $C_{dl}$ in parallel was used. $R_c$ corresponds to the resistance of the electrolyte, $R_p$ to the polarisation or charge transfer resistance of the sample and $C_{dl}$ to the double layer capacitance formed at the interface between the electrolyte and the sample surface. In this study the polarisation resistance $R_p$ is of greatest interest. In general, the polarisation resistance is not a good measure of corrosion rate as with Mg the fundamental requirements for Tafel extrapolation are not fulfilled; the b-values for the single anodic and cathodic reaction, which are required for Tafel extrapolation, are not easy to determine [37]. However, in addition immersion tests were performed indicating the same tendencies as seen in EIS. Figure 2.3.2a features the polarisation resistances of the polished samples depending on heat treatment and electrolyte. All samples exhibited impedance values of around 2000 $\Omega$ cm$^2$ in AP and 40–100 $\Omega$ cm$^2$ in SBF. The heat treatment generated no remarkable difference in the polarisation resistance of the bulk material. The same applied to the cross-section direction: transversal and longitudinal cross-sections produced similar performances. The composition of the electrolyte, however, influenced corrosion resistance significantly: samples tested in AP corroded much more slowly than those in SBF. Measurements in 3.5 wt.% NaCl solution showed a polarisation resistance between that in the body-similar fluids. The Bode plot of a polished SHT sample in AP (Fig. 2.3.2b) shows a typical behaviour of an actively dissolving surface with an increase in impedance at very low frequencies.

For polarisation resistance the values for the plateau region were taken. As the Bode plots of all polished samples resembled each other, exemplarily the Bode plot of one specimen is shown. For all samples, only one time-constant was observed. Besides the homogenisation of the distribution of Y (and partially Nd) in the bulk, the heat treatments performed in this study also caused the formation of an approximately 800 nm thick surface oxide layer, mainly consisting of $Y_2O_3$, as indicated by AES depth profiles (Fig. 2.3.3b). The layer thickness was similar for the SHT and the T6 state. Polished samples indicated an approximately 20 nm thick naturally-formed MgO
layer on the surface (Fig. 2.3.3a). The Auger sputter depth was calibrated with a Ta$_2$O$_5$ sample and the different sputter yields for the various oxides were not considered. Nevertheless, it is possible to estimate the thickness of the layers as tendencies do not change.

![Figure 2.3.2](image1.png)

**Figure 2.3.2:** (a) Polarisation resistance of polished samples influenced by heat treatment (T5, SHT and T6 state) and electrolyte (SBF, AP, NaCl). (b) Bode plot of a polished SHT sample in AP. ■ corresponds to the impedance values, ▲ to the phase shift.

![Figure 2.3.3](image2.png)

**Figure 2.3.3:** AES depth profiles of (a) a polished and (b) a SHT sample.

The EIS measurements of samples in the oxidised state showed generally a very high polarisation resistance with average values of $3.5 \cdot 10^5 \Omega$ cm$^2$ and $8 \cdot 10^4 \Omega$ cm$^2$ for SHT samples in AP and SBF, and $2 \cdot 10^6 \Omega$ cm$^2$ and $2 \cdot 10^5 \Omega$ cm$^2$ for T6 samples in AP and SBF, respectively (Fig. 2.3.4). However, the scatter was quite large, and therefore the maximum and minimum values are also indicated in the graph. The ageing process
at 250°C for 16 h after the SHT increased the corrosion resistance further, although there was hardly any difference between the samples in terms of layer thickness and composition, as measured by AES. Again, the electrolyte played an important role and the same tendencies as for the polished samples were observed. However, in both solutions approximately one out of three measurements carried out for each state showed a breakdown of the impedance values measured at lower frequencies (Fig. 2.3.5b) and signs of localised corrosion attacks were visible on the surface after the measurement (photographic insert in Fig. 2.3.5b). The results of these measurements were not taken into account in comparing the different treatments, as no definite polarisation resistance could be determined.

![Polarisation resistance of oxidised samples](image)

**Figure 2.3.4:** Polarisation resistance of oxidised samples, dependent on heat treatment and electrolyte. • indicates the minimum and maximum values per measurement series.

To compare, Figure 2.3.5a shows the Bode plot of an oxidised SHT sample with macroscopically homogeneous degradation. The Bode plot of the oxidised samples without local corrosion attacks had a similar shape. The evolution of impedance over the duration of 24 h in SBF is illustrated in Fig. 2.3.6. The polarisation resistance of the polished sample increased with time (Fig. 2.3.6a), from a value of approximately 100 Ω cm² to 550 Ω cm² after 24 h. A layer of corrosion products and salt deposits from the solution formed which caused the degradation process on the surface to slow. The polarisation resistance after 24 h was still lower than that in the oxidised sample, but was remarkably high compared to the other polished WE43 samples in
SBF. The impedance values of the oxidised sample (Fig. 2.3.6b) decreased with time, from $2.5 \times 10^5 \ \Omega \ \text{cm}^2$ to approximately $1-1.5 \times 10^4 \ \Omega \ \text{cm}^2$ after 24 h. Obviously degradation of the oxide layer proceeded faster than the formation of a protective corrosion product layer.

Figure 2.3.5: Bode plots of oxidised SHT samples in AP (a) without and (b) with occurrence of localised corrosion. ■ corresponds to the impedance values, ▲ to the phase shift. The photographic inserts reveal the surface after EIS.

Figure 2.3.6: Development of impedance over 24 h (a) of a polished SHT sample; and (b) of an oxidised SHT sample in SBF.

Strained samples

Straining of the polished samples led to an “orange peel-like” roughening of the polished surface and to the formation of cracks in the oxide layer, which were approximately perpendicular to the straining direction in the case of oxidised samples (Fig. 2.3.7). The cracks of the 9% strained samples appeared to be a little longer and wider than those in the samples strained to 5%.
A summary of the polarisation resistance values on strained samples measured in AP is listed in Fig. 2.3.8. Straining of the oxidised material generated a decrease in the impedance values from $3.5 \cdot 10^3 \ \Omega \ \text{cm}^2$ for the intact oxide layers to $1\sim1.5 \cdot 10^4 \ \Omega \ \text{cm}^2$ for the ruptured oxide layers. No large difference was apparent between the different strains applied. Straining of the polished samples did not noticeably influence the electrochemical properties; all samples featured approximately the same value of about $2 \cdot 10^3 \ \Omega \ \text{cm}^2$ independent of the straining. Again, measurements carried out in SBF gave lower impedance values compared to AP, but displayed the same tendencies. The Bode plots resembled those of the polished samples.

Optical observations of the strained oxide layers after EIS revealed that the cracks were more visible due to the corrosion process and were slightly more “attacked” than the surrounding surface. The polished samples exhibited a similar corrosion attack to
that found for the unstrained samples. On the microscopic scale (Fig. 2.3.9), it could be observed that local corrosion attacks started at the cracks. These attacks were not very deep and proceeded along the interface between substrate and oxide, undermining the oxide layer. A similar behaviour was found for intact oxide layers. However, there the oxide layer was first penetrated and then undermined. With time, the cracked oxide layer sections in between the cracks fell out (Fig. 2.3.9b, sample immersed in SBF for 7 days). EDX measurements of the corroded area and on the surface of the samples revealed the presence of Ca, P and O.

![Figure 2.3.9: SEM micrographs of two oxidised SHT samples strained to 5% (a) after EIS measurement and (b) after 7 days of immersion in SBF.](image)

**Discussion**

**Unstrained samples**

To understand the microstructural changes in WE43 during heat treatment, thermodynamic calculations were performed using the Pandat software package (database PanMg7) [31]. Calculations at non-equilibrium after Scheil, simulating the casting process, demonstrate the formation of Nd- and Y-rich constituents from the melt, presumably Mg54Nd5 (≈3.5% phase fraction) and Mg24Y5 (≈2.5%). These constituents were aligned in extrusion direction during the deformation process. The thermodynamic calculations of the constitutional changes during the heat treatments at 525°C (equilibrium conditions were assumed) feature the formation of only Nd-rich constituents (≈3.5% Mg54Nd5) from the melt. Y-rich precipitates are calculated to form from solid solution at temperatures below 300°C. Unfortunately, for the Mg–Y–
RE system this database is not complete, and no ternary phases, which were observed by other researchers [21, 38], are included.

For our study these calculations predict the following Y distribution within the samples: SHT samples exhibit the maximum amount of Y in solid solution; T6 samples feature a slightly smaller amount of Y in solid solution due to the formation of a Y-containing hardening phase during the ageing process at 250°C; and T5 samples an even smaller amount due to the presence of Y-containing constituents and the formation of the Y-containing hardening phase. The element Y is known to increase the corrosion resistance of magnesium alloys via its passivating effect on the metal surface [29]. In addition, homogenisation of the Y distribution as well as Y-rich regions within the matrix were found to enhance corrosion resistance [16]. However, despite these differences in microstructure and Y content in solid solution, EIS in SBF and AP did not reveal a noticeable difference in degradation performance among the various heat treatment states. A possible explanation is the high reactivity of the polished surfaces, generating rapid degradation where the difference in microstructure cannot be distinguished. Furthermore, in this pH region, passivation is difficult and the presence of Y might not be sufficient. Additionally, some Nd-rich precipitates present in all investigated heat treatment states may act as microscopic galvanic cells and thus initiate corrosion of the material. Similar behaviour was observed by Valente [39], who reported that in cast WE43 the corrosion attack in 3.5 wt.% NaCl started at these Nd-rich compounds. They might dominate the dissolution process and mask the influence of the Y distribution.

As the thermal oxide layer is left on the metal surface, the polarisation resistance increases by 2–3 orders of magnitude. Via the SHT an approximately 800 nm thick protective yttrium oxide layer forms. Ageing treatment at 250°C after SHT increases the corrosion resistance even further without remarkably increasing the oxide layer thickness. Possibly, small defects in the oxide layer, which formed during water quenching after the SHT because of the thermal shock (due to the different thermal expansion coefficients of the bulk and the oxide), became less reactive due to the formation of a thin oxide film during ageing. As for the SHT samples, however, the
same occasional appearance of localised corrosion occurs in T6 samples, leading to a breakdown in the measured impedance. The reason for the occurrence of localised corrosion is attributed to the existence of structural inhomogeneities in the oxide layer, which may originate from the quenching. Furthermore, by SEM analysis of a broken sample (Fig. 2.3.10) it can be seen that the oxide layer seems to consist of a “columnar-grain-like” structure perpendicular to the surface, in-between which local corrosion attack may start.

Figure 2.3.10: (a) and (b) Cross-section of an oxide layer.

The 24 h EIS measurements of the polished and oxidised SHT samples reveal a contrary time-dependent behaviour. The polarisation resistance of the polished samples continuously increases with time, while that of the oxidised samples decreases. This gradual increase in the impedance values is the result of a protective layer of corrosion products and amorphous calcium phosphates deposited from the electrolyte. Similar behaviour was observed by other authors [25, 40, 41]. Zucchi et al. investigated the long-term impedance behaviour of WE43 in diluted solutions and found that a passivating layer was formed when certain ions were present [41]. Tests in simulated body fluid (m-SBF) performed by Rettig and Virtanen featured the formation of amorphous corrosion layers [25, 40]. It is observed that the corrosion layers formed protect the bulk material less than the thermal oxide layers. In the oxidised samples the degradation of the oxide layer due to penetration dominates and
proceeds faster than the formation of the corrosion product layer, leading to a decrease in impedance.

For both the oxidised and the polished samples the remarkable influence of electrolyte composition is evident. SBF is the most aggressive solution among those tested, followed by 3.5 wt.% NaCl solution and AP. The composition and the pH of the solutions play an important role in the degradation process. For instance, Cl\(^-\) ions are known to aggressively attack magnesium \([24]\), while HCO\(_3\)\(^-\) ions were found to dissolve the hydroxide layer formed on the surface and therefore decrease corrosion resistance \([42]\). And the lower the pH value of the electrolyte the more active magnesium is. In addition, a buffered solution generates a more constant surface pH and thus influences the degradation performance \([40]\). On the other hand, Ca\(^{2+}\) ions are deposited on the surface when HPO\(_4\)\(^{2-}\) ions are present \([25]\). Since body-similar fluids are very complex solutions, all these factors are relevant. The dissolution of the material, the formation of the corrosion layer and the deposition of elements from the electrolyte also occur at the same time and influence the overall degradation process. In our study, the higher initial pH of AP compared to SBF and the fact that AP is less buffered are the most influencing factors slowing the degradation behaviour in AP.

**Strained samples**

Plastic deformation, which may occur during the implantation process, could induce defects thereby reducing the protective effect of the thermal oxide layer. According to the higher polarisation resistance compared to that of the polished state observed (Fig. 2.3.8), it seems that despite the cracks induced by straining the oxide layer still fulfils its protective function on the covered surface. No major difference could be observed between the samples strained to 5 and 9%. It can be assumed that lower strains, as expected during implantation, might also reduce the protective influence of the oxide layer to a certain amount. However, so far it is not known how much the oxide layer suffers during implantation, and therefore (to be “on the safe side”) high strains were chosen. The initial assumption that the protective oxide layer is damaged during plastic deformation, producing decreased corrosion resistance, was confirmed. However,
macroscopically no severe corrosion attacks were observed, which lead to dissolution of the material even more rapidly than in the polished state and which often happens in other coating systems. Microscopically, it could be shown that the dissolution front was not uniform. Local corrosion attacks started at the cracks and led to an undermining of the oxide layer, which with time even led to a falling out of layer sections in between the cracks. EDX measurements revealed the presence of Ca and P on the oxidised surface and on the locally corroded sites. These findings were also reported in [25] and are described there in more detail.

**Conclusions**

In the Mg–Y–Nd system, the distribution of Y within the microstructure does not strongly affect corrosion performance as measured by electrochemical impedance spectroscopy. Oxide layers formed at high temperatures may provide a certain protection when they are not penetrated by localised corrosion attack. Degradation of these oxide layers occurs by penetration and the resulting undermining of the oxide layer.

Despite the fact that all tests were performed in SBF and AP which are both body-similar fluids, the degradation rates measured by EIS varied by approximately one order of magnitude. The trends were the same in both electrolytes. By *in vitro* testing it is not possible to exactly predict the *in vivo* degradation behaviour. But it can be assumed that trends will be similar.

Immersion in electrolyte solution for a long period of time caused an increase of polarisation resistance and a surface layer of degradation products and salt deposits to form on polished samples; these were able to protect the underlying metal to a certain extent. In oxidised samples the polarisation resistance decreased with time due to the penetration of the oxide layer.

Plastic strain possibly occurring during the implantation of an implant and the connected rupture of the oxide layer impairs the performance of the material. However, the degradation seemed macroscopically homogeneous, no visible local
corrosion attacks occurred and the specimens degraded more slowly than the polished samples. On a microscopic length scale local corrosion attack starts at the cracks and proceeds by undermining the oxide layer.

To conclude, thermal surface treatments improve the biodegradation resistance of WE43 in SBF and AP. These oxide layers formed protect the metal underneath to a certain extent even if they contain cracks, which might evolve from the implantation process, and perform better than the polished counterparts.
2.4 Corrosion behaviour under static uniaxial tensile load of plasma-electrolytic oxidised (Magoxid-coat®) WE43

Introduction

Besides thermal treatments, anodising is another way of depositing a corrosion-inhibiting oxide coating. Thereby a stable oxide layer is generated on the metal surface by an electrolytic process. The Magoxid-Coat® tested in this study was produced by AHC Oberflächentechnik Holding GmbH, Germany. This coating technique is also known as anodic oxidation with spark discharge, micro-arc oxidation, anodic spark deposition, plasma-electrolytic oxidation or plasma-chemical oxidising [43]. Thereby, the sample is connected as the anode in a slightly alkaline electrolyte and a voltage of 100–400 V is applied leading to the generation of oxygen plasma in the electrolyte near the substrate surface. During discharging of the plasma (sparks), the metal surface partially melts and reacts immediately with the oxygen present, causing a well-adhered crystalline oxide ceramic on the surface of the metal. Basically, the layer forms stepwise by partial anodes; in the area around the base of the original spark new sparks are activated due to the high temperature from the original spark leading to formation of new oxide and, at the end, to a continuous ceramic layer. Plasma-electrolytic oxidised surfaces consist of three layers, a barrier layer and two oxide ceramic layers differing in porosity [44], as shown schematically in Fig. 2.4.1. The outer layer is highly porous and can serve as a base for further painting, while the inner one has a low porosity preventing corrosion. According to Kurze [44] 50% of the crystalline coating forms below the original metal surface and 50% above it. The main components of the electrolyte used by AHC are mineral acids (fluoric, phosphoric and boric acid) and organic substances.

It is the goal of this study to examine the corrosion behaviour of uncoated and Magoxid-Coat® coated samples with various oxide thicknesses in a simulated body fluid. As the implant might be exposed to stress, the influence of load on the
degradation performance was also taken into account. Thereby, the focus lay on the analysis of the time to fracture of the samples and the corroded samples.

Figure 2.4.1: Schematic illustration of a Magoxid-coat® (re-drawn from [44]).

**Experimental**

For corrosion tests under static uniaxial tensile load, cylindrical tensile test specimens of 3.5 mm in diameter and 21 mm in parallel length were machined from an extruded WE43 bar. On some samples Magoxid-Coat® layers with thicknesses of approximately 5, 10 and 25 μm were deposited by AHC Oberflächentechnik GmbH. The coating morphology was analysed by scanning electron microscopy (SEM, Hitachi SU-70) at a voltage of 5 kV and a working distance of 15 mm. Cross-sections of the coatings were produced and evaluated by a Focused Ion Beam system (FIB, Zeiss NVision 40) using Ga⁺ ions for milling of the surface at the university’s electron microscopy centre (EMEZ).

The tests under load were performed in a creep testing machine (Fig. 2.4.2a). The temperature-controlled chamber – the temperature was set to 40°C to achieve a SBF temperature of 37°C – contains the samples. Each sample was connected to a horizontal rod, where the load was attached. The life time measurement started with the loading of the sample and ended at un-loading (i.e. failure of the sample). The parts of the sample holder in contact with the sample were sealed with Zapon lacquer to avoid galvanic corrosion. Then, the samples were ultrasonically cleaned in isopropanol and placed in the sample holder, as depicted in Fig. 2.4.2b, and the hole in
the container sealed with silicone. The plate underneath the container reduces the weight on the sealing and avoids leakage. Then, the samples were mounted into the testing device, the containers filled with 50 ml SBF, which was prepared according to [20] and pre-heated to 37°C, and which corresponds to a SBF volume to sample surface area ratio of 20–25 ml cm⁻². Then, the weights were loaded. To avoid evaporation, the containers were covered with a polymer film and wrapped with aluminium foil. The SBF was changed on a regular basis. For the polished samples two different weights corresponding to 60 and 80% of the yield strength (R_{p0.2} ≈ 250 MPa), i.e. 150 and 205 MPa, respectively, were chosen, for the coated samples only one load (0.6 R_{p0.2}) was evaluated. Per condition, at least three samples were tested.

The rupture life of the specimens was measured by the testing device. The fracture surfaces and gauge sections were evaluated by stereo loupe and SEM. For comparison, immersion testing in SBF of non-loaded uncoated and Magoxid-coated plates of 10 μm in coating thickness was done using the hydrogen evolution method [19], and the corrosion performance of the non-loaded samples was evaluated.

![Image](image.png)

Figure 2.4.2: (a) Photograph of the testing device and (b) schematic illustration of the sample holder.
Results

SEM micrographs of the coating’s surface (Fig. 2.4.3a, b) indicate a very porous outer layer with pores in various sizes. At higher magnification sharp micro-cracks between the pores are visible for all thicknesses, even in the non-loaded condition. It seems that the coating thickness has no influence on pore size. Cross-sections of the coatings reveal a rough interface between the substrate material and the coating (Fig. 2.4.3c, d) and pores in various sizes and shapes.

![SEM micrographs of the coating’s surface](image)

Figure 2.4.3: SEM micrographs of Magoxid-Coat® coated WE43 of (a) a 10 μm and (b) a 5 μm thick coating; and (c, d) cross-sections of a 5 μm thick coating prepared by FIB.

Immersion testing of non-loaded WE43 samples indicates that the coating initially provides protection and suppresses hydrogen evolution. With time and penetration of the coating an increase in gas volume is observed, as shown in Fig. 2.4.4a. There, the ratio of evolved hydrogen of coated versus polished samples is plotted. The onset of enhanced corrosion and thus break-down of the coating varied within the test series, as indicated by the vertical bars showing the measured H₂ range. After 10 days of immersion the coating was still intact; after 20 days it was penetrated and consequently
corrosion had started, as represented by the augmented amount of hydrogen. The degradation behaviour of Magoxid-coated WE43 is similar to that of thermal oxide layers, and is schematically depicted in the insert in Fig. 2.4.4a.

The rupture lives of all samples and their average values are plotted in Fig. 2.4.4b. Uncoated samples under a load of 150 MPa had longer rupture lives than those loaded with 205 MPa. On average, they also lasted longer than the coated samples tested under the same weight. The coating thickness slightly influenced the rupture lives; samples with a 5 or 10 μm thick layer survived longer than those covered with a 25 μm thick layer. However, for all samples a large scatter in rupture life was measured. In addition, in uncoated samples which were exposed to the solution for a relatively long time, galvanic corrosion with the steel sample holder occurred because the Zapon lacquer loosened with time.

![Graph](image)

**Figure 2.4.4**: (a) Time-dependent ratio of evolved hydrogen of non-loaded Magoxid-coated and uncoated WE43 samples in SBF and their schematic corrosion performance (insert) evaluated by hydrogen gas evolution; and (b) rupture lives of the various samples.

Looking at the corroded samples tested under load, the uncoated samples generally degraded relatively homogeneously over their entire length and a thick layer of corrosion products formed on the surface (Fig. 2.4.5d and f). The fracture surfaces appeared rough and were also covered with corrosion products, as seen in Fig. 2.4.5a and f. In some samples cracks close to the fracture site and perpendicular to the load direction were observed (Fig. 2.4.5f). Figure 2.4.5e and g display broken Magoxid-coated samples having various local corrosion sites along the entire gauge length.
These attacks were often perpendicular to the loading direction, probably where the coating cracked due to the applied load. The images of the fracture surfaces (Fig. 2.4.5b, c) reveal various local corrosion attacks, several crack initiation sites as manifested in the multilevel fracture surfaces, and signs of forced fracture (visible by stereo loupe and SEM). The fracture mode (intergranular or transgranular fracture) could not be evaluated as all surfaces were heavily corroded.

![Images of fractured samples](image)

Figure 2.4.5: (a-g) Images of fractured samples after corrosion testing under static uniaxial load; uncoated (a, d, f) and Magoxid-coated samples (b, c, e, g) analysed by stereo loupe (a, b, f, g), photography (d, e) and SEM (c). The diameter of the samples is approximately 3.5 mm.

**Discussion**

This study shows that the Magoxid-coating protects the Mg alloy underneath it when it is not subjected to load. Other than in uncoated samples, the hydrogen evolution at the beginning of immersion in SBF (i.e. the first days) was suppressed. However, with time its protective ability decreased due to local penetration of the ceramic layer, as revealed by accelerated hydrogen gas evolution. Under static uniaxial tensile loading as
performed in this study and considering the rupture lives, however, the coated specimens generally performed worse than the uncoated specimens and usually broke first. Moreover, the scattering in rupture lives was large. This is assumed to result from two issues; firstly, during corrosion of non-loaded Mg alloys a scattering in corrosion rate was observed for uncoated and coated specimens; and secondly, the time for local corrosion attacks to occur in coated samples is not possible to predict. The latter point is relevant for coated samples, where local corrosion attacks and multiple crack initiation sites are responsible for early sample fracture. However, as in the loading set-up the evolved hydrogen cannot be measured, it is impossible to tell how much the samples corroded and how much H₂ gas evolved before fracture.

Analysis of the parallel sections of broken specimens and their fracture surfaces indicates that the uncoated samples corrode in a homogeneous way forming a thick layer of corrosion products over the entire surface. It is assumed that they break eventually due to degradation and the resulting homogeneous reduction in cross-section. The coated samples, on the other hand, featured many local corrosion attacks in the ceramic coating along the gauge length. In addition, the multilevel and rough fracture surfaces evoked the presence of various crack initiation sites. Moreover, signs of forced fracture were visible, which originates from the inhomogeneous reduction in cross-sectional area due to local degradation. Even in the area of forced fracture, it was observed that several cracks were initiated and propagated prior to fracture. In addition, the rupture lives of the coated samples are shorter than those of the uncoated. Thus, it can be concluded that the coating induces stress corrosion cracking. However, from the heavily corroded samples and fracture surfaces it was not possible to determine whether the fracture mode was transgranular, intergranular or mixed. In a study on the stress corrosion cracking of plasma-electrolytic oxidation treated (PEO) and polished cast Mg alloy AM50, tested by slow strain rate tensile tests, comparable results were found, i.e. in the PEO state cracking of the coating was responsible for SCC [45]. It is assumed that the sharp micro-cracks in the coating offer sites for crack initiation and corrosion attacks. Similar to (15 μm) thick anodised coatings reported in [46], the cracking in the layer might be induced by stress concentrations between the
anodised layer and the substrate due to the uneven interface, because of the occurrence of notches in the substrate from the coating process as seen in Fig. 2.4.3c and d, because of local uneven regions in the coating or because of pores in the anodised layers. By applying load the cracks can easily propagate through the porous and the dense ceramic layers and into the metal. Thereby, metal gets exposed to the electrolyte and local corrosion attacks can take place. Other than in [46], where in dynamic fatigue tests samples with thin coatings of 1 and 5 μm performed better than those with a 15 μm thick coating, it is not possible to tell if the coating thickness influences the fracture times, due to the large scatter in the data.

A similar fracture behaviour as observed in this study has also been reported for Magoxid-coated cast WE43 in fatigue tests [47]. There, the coating also led to a much rougher fracture surface compared to non-coated specimens due to crack initiation and growth at multiple sites. This has been ascribed to stress concentrations at the surface due to the presence of pores and discontinuities. In addition, due to the ceramic character of the layer unhindered crack growth could occur through the coating and into the metal. This mechanism was described by Suresh et al. in more detail [48]. A crack, initiated in a ceramic coating, moves into the metal underneath by first delaminating the interface and then reinitiating at another site of the interface to advance through the metal.

From the results obtained it can be concluded that Magoxid-coated screws may be a suitable implant material for applications in the human skeleton. Hydrogen evolution at the beginning of immersion is suppressed by the coating avoiding further irritation of the injured tissue by the gas. The rupture life was around 20 days, but the laboratory conditions chosen for the static uniaxial loading tests were severe, i.e. a high load of 0.6 $R_{p0.2}$ and corrosion under constant load, which is more severe than the one under constant deflection [49]. Thus, it can be assumed that the implant is less stressed in the body. Also, the corrosion testing under load as performed in this study was not according to a standard procedure. But, it is suitable for a first estimation and comparison of the corrosion performance under static load of differently coated and non-coated WE43 specimens – the purpose of our work.
Conclusions

To conclude, it has been shown by immersion testing in SBF that the Magoxid-coat® deposited by AHC Oberflächentechnik resulted in improved degradation resistance and consequently less hydrogen evolution at the beginning of the test – when samples were exposed in the non-loaded condition. Under static uniaxial tensile loading, however, the coated samples fractured earlier than their uncoated counterparts due to stress corrosion cracking. Micro-cracks in the coating, which already existed in the non-loaded condition, and surface discontinuities in the substrate, that were formed by the Magoxid-treatment, are the probable cause, as they are perfect crack initiation sites. Under loading condition, the cracks can propagate through the ceramic coating and into the metal causing exposure of metal to the electrolyte and the formation of crack initiations and local corrosion attacks, which result in a decrease in rupture life. The rough fracture surfaces confirm the existence and propagation of multiple cracks. However, in the set-up used a worst-case scenario was produced and it is assumed that the loads seen by the implant in the body are lower and thus implants coated in this way should survive longer.
2.5 Electroplating of Zn on WE43

**Introduction**

In electrochemical plating a metallic coating is deposited on a work piece by reducing a metal from a metal salt solution onto the surface of the substrate. A distinction can be drawn between electroless plating, where no external current is necessary to reduce the metal on the substrate, and electroplating, where an electric current is required. Electroplated Mg alloys are often used in the aerospace, automobile, computer and electronics industries for aesthetic reasons, improved corrosion and wear resistance, electrical conductivity, optical reflectance or solderability [1, 50], e.g. electroless Ni platings for satellites, laptops or electronic housings or Cu–Ni–Au electroplatings for satellite electronics housings [51]. In this study, however, the metallic Zn platings should protect the Mg implant straight after implantation, even if the implant is plastically deformed. In contrast to ruptured oxide layers, the Zn coating should not lose its full protective function because of its metallic character and the accompanied improved deformation behaviour.

In the electroplating process, firstly a chemical pre-treatment is necessary in order to obtain good adhesion between the coating and the base material. Thereby, the surface oxides and hydroxides, which form upon exposure of magnesium in air or humidity and which negatively influence the adhesive strength, need to be removed. Secondly, a metallic underlayer (undercoat), which is less active than the substrate material (often a Zn and Cu or Ni film), should be deposited [1]. Then, the desired metal is electroplated.

The chemical pre-treatment consists of various steps [52]: (i) cleaning of the surface; (ii) acid pickling to remove surface oxides or replace them by light oxides, which can easily be removed in the next step; (iii) acid activation to remove residual oxides and to slightly etch the metal in order to decrease surface potential differences and thus improve the uniformity of the zinc immersion coating; and (iv) zinc immersion to form a thin Zn layer to prevent re-oxidation of Mg. The chemical pre-
treatment is crucial for good adhesion of the electroplated layer. Due to the high reactivity of Mg alloys the development of an appropriate pre-treatment is difficult and time-consuming. Another complication is the dependence of the pre-treatment on the alloy composition due to the second phases present; a suitable pre-treatment for one Mg alloy may work for another, but this is not for sure. In literature, some pre-treatment processes are described, where a Zn undercoat is deposited, e.g. in [53-56]. However, often toxic Cr-containing pickling solutions were used [56] and often additional electroless Ni(−P) platings or Cu films were deposited [52-54] due to their higher stability compared to Zn underlayers. Such coatings, however, are not suitable for the purpose of medical applications, as Cu and Ni are not degradable and only tolerated by the body in very limited amounts.

In this study, firstly, a chemical pre-treatment process prior to electroplating of Zn was developed for WE43 and characterised. Secondly, two different electroplating baths, an acidic and an alkaline bath, were evaluated and their influence on the layer morphology characterised. In addition, to improve the adhesion between the coating and the substrate by formation of a diffusion zone, heat treatments were performed. Last, the corrosion behaviour of Zn-coated WE43 was evaluated in body-similar fluid.

Experimental

Sample preparation

For the experiments, WE43 discs of 25 mm in diameter and approximately 2 mm in thickness were cut from an extruded bar and ground with emery paper of grit 4000 (SiC particles). For the chemical pre-treatment consisting of the four steps cleaning, pickling, activation and zinc immersion, various solutions were evaluated. For the first sample series, a chemical procedure used by CEST (competence centre for applied electrochemistry GmbH, formerly ECHEM) was tested. There, the samples were first cleaned in 50 g l⁻¹ NaOH and 10 g l⁻¹ Na₃PO₄·12 H₂O (pH: 13, 5 min at 60°C), then etched in 100 g l⁻¹ NaOH (pH: 13, 20 s at room temperature), pickled in 1% H₂SO₄ and immersed in the zinc immersion solution (28 g l⁻¹ ZnSO₄, 97 g/l K₃P₂O₇, 3 g l⁻¹
LiF, 5 g l⁻¹ Na₂CO₃, pH: 9, 3 min at 65°C). It turned out that this procedure is not suitable for WE43, as the Zn undercoating did not cover the entire substrate surface and caused problems during electroplating. The final electroplated Zn layer was inhomogeneous, with bubbles formed underneath the layer, and consequently, the adhesion was insufficient. Thus, this procedure was not further taken into account.

For the following sample series, all specimens were first ultrasonically cleaned in isopropanol. Then, various pickling procedures, which varied in solution composition and immersion time, were evaluated, as listed in Table 2.5.1. p.1 and p.4 were reported in literature to be appropriate pickling solutions for Mg [57], p.2 was used for electroless chemical polishing and p.3 is an etchant for Mg alloys [58]. The two latter solutions were so far not considered for pickling. Activation and zinc immersion were each performed in one solution only (Table 2.5.2), to not significantly increase the number of parameters. In addition, bath compositions from literature resembled each other. After each step the samples were rinsed in deionised water and ultrasonically cleaned in isopropanol. In order to improve the quality of the Zn underlayer some samples were re-activated and Zn-immersed for a second time to remove loose Zn deposited during the first chemical pre-treatment and to re-deposit it. Moreover, a few tests using the activation solution described in [57] were performed, but they did not improve the quality of the Zn undercoats.

<table>
<thead>
<tr>
<th>Denotation</th>
<th>Pickling solution composition</th>
<th>Immersion parameters</th>
</tr>
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<tbody>
<tr>
<td>p.1</td>
<td>900 ml l⁻¹ H₃PO₄ (84%), pH &lt;1</td>
<td>0.5, 1, 3 and 10 min at RT*</td>
</tr>
<tr>
<td>p.2</td>
<td>100 g H₃PO₄ (crystallised), 100 ml ethanol</td>
<td>0.5 min at RT*</td>
</tr>
<tr>
<td>p.3</td>
<td>10 ml l⁻¹ HNO₃, 750 ml/1 ethanol</td>
<td>0.5 min at RT*</td>
</tr>
<tr>
<td>p.4</td>
<td>200 ml l⁻¹ CH₃COOH, 50 ml/1 NaNO₃</td>
<td>0.5, 2 and 10 min at RT*</td>
</tr>
</tbody>
</table>

* RT: room temperature

For electroplating, a weakly acidic and a cyanide-free alkaline electrolyte from SurTec Deutschland GmbH were used, respectively [59, 60]. Their compositions are given in Table 2.5.2. For electroplating, the sample was connected as cathode and a pure Zn sheet as anode using clamp-connections. Electroplating was done at room
temperature for various times, with and without bath movement and at a current density of 2±1 mA cm⁻² in the acidic and 2±0.5 mA cm⁻² in the alkaline bath. To evaluate the quality of the chemical pre-treatment, electroplating in the more aggressive acidic bath was done for various times (3, 10, 15, 30, 45 and 60 min). Once a suitable chemical pre-treatment was established, Zn coatings were deposited either from the alkaline or the acidic electrolyte or in a combined process (first in the alkaline, then in the acidic bath). During the course of this study problems were encountered with the homogeneity of acidic electroplated coatings, probably due to corrosion of the Mg substrate when immersed in the electrolyte. Therefore, alkaline electroplating was done prior to acidic electroplating to produce an additional undercoat. It is assumed that by alkaline electroplating the homogeneity of the layers is improved as at high pH values Mg is immune. For further improvement of the adhesion, heat treatments were performed, which lead to an intermediate diffusion zone. They were done at 300°C in an air-circulating furnace for various times (5 min; 1, 5 and 20 h).

Table 2.5.2: Bath composition and process parameters for activation, zinc immersion, alkaline and acidic electroplating (e.p.), respectively.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Activation</th>
<th>Zinc immersion</th>
<th>Alkaline e.p.</th>
<th>Acidic e.p.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>65 g l⁻¹ K₃P₂O₅</td>
<td>30 g l⁻¹ ZnSO₄</td>
<td>120 g l⁻¹ NaOH</td>
<td>85 g l⁻¹ ZnCl₂</td>
</tr>
<tr>
<td></td>
<td>15 g l⁻¹ Na₂CO₃</td>
<td>120 g l⁻¹ K₃P₂O₅</td>
<td>12.5 g l⁻¹ ZnO</td>
<td>210 g l⁻¹ KCl</td>
</tr>
<tr>
<td></td>
<td>7 g l⁻¹ KF</td>
<td>7 g l⁻¹ NaF</td>
<td>50 g l⁻¹ Na₂CO₃</td>
<td>22.4 g l⁻¹ H₃BO₄</td>
</tr>
<tr>
<td>pH: 11</td>
<td>3 g l⁻¹ Na₂CO₃</td>
<td>pH: 10</td>
<td>SurTec704 additives</td>
<td>SurTec757 additives</td>
</tr>
<tr>
<td>Time</td>
<td>2 min</td>
<td>3 min</td>
<td>5, 15, 30, 60 min</td>
<td>3, 10, 15, 30, 45, 60 min</td>
</tr>
<tr>
<td>Temperature</td>
<td>70–75°C</td>
<td>80–85°C</td>
<td>room temperature</td>
<td>room temperature</td>
</tr>
<tr>
<td>Current</td>
<td>–</td>
<td>–</td>
<td>2±0.5 A dm⁻²</td>
<td>2±1 A dm⁻²</td>
</tr>
<tr>
<td>Reference</td>
<td>[53]</td>
<td>[57]</td>
<td>[60]</td>
<td>[59]</td>
</tr>
</tbody>
</table>

**Characterisation**

First, the feasibility of the various chemical pre-treatments was evaluated with regard to the quality of the acidic electroplated Zn layer. During chemical pre-treatment and after electroplating the sample surfaces were analysed by optical microscopy (OM), scanning electron microscopy (SEM, CamScan, Zeiss LEO 1530 Gemini and Hitachi
SU-70), energy dispersive X-ray spectroscopy (EDX, NORAN instruments and Oxford instruments) and X-ray diffraction (XRD, PANalytical). To analyse the cross-sections of the electroplated samples (with and without heat treatment), they were embedded in Bakelite, ground and polished and investigated by OM and SEM. In addition, EDX element mappings were executed.

The degradation performance was assessed by immersion testing in simulated body fluid [20] using the hydrogen evolution method by Song et al. [19]. The amount of hydrogen evolved per cm² surface area of polished WE43 (as reference), Zn-immersed and Zn-electroplated samples was compared with each other. In the electroplated samples there was a non-coated area from the clamp-connection. For immersion testing this non-coated area was either sealed with silicone or cut off followed by sealing of the cut edge.

Results

Evaluation of the chemical pre-treatment

Table 2.5.3 summarises the results from the pre-treatment feasibility study. It is obvious that successful electroplating depends on the quality (i.e. homogeneity) of the Zn underlayer produced by the chemical pre-treatment; for WE43 not all procedures led to the deposition of a (homogeneous) Zn undercoat, and thus the quality of the acidic electroplated Zn layer suffered. Moreover, the pre-treatment is alloy-dependent; while the pickling solution p.4 containing glacial acetic acid was not appropriate for WE43, it worked for ZK31. For WE43 successful electroplating was achieved when using the pickling solutions p.1, p.2 and p.3, with slight variations in coating quality. For pure Mg so far no suitable chemical pre-treatment was discovered. For WE43 the best results were achieved using the following procedure: (i) ultrasonic cleaning in isopropanol; (ii) immersion in pickling solution p.1 (900 ml l⁻¹ H₃PO₄ (84%)) for 30 s at room temperature; (iii) activation for 2 min at 70–75°C; and (iv) zinc immersion for 3 min at 80–85°C. Thus, this process was investigated in more detail and used for the production of further samples.
Table 2.5.3: Pre-treatments performed on WE43, ZK31, AZ31 and pure Mg and their influence on electroplating. ✓ indicates successful electroplating, where the entire surface is covered by Zn, - indicates that plating was not possible or that the electroplated layer was inhomogeneous.

<table>
<thead>
<tr>
<th>Pre-treatment step/ Material</th>
<th>Pickling p.1</th>
<th>p.2</th>
<th>p.3</th>
<th>p.4</th>
<th>Activation</th>
<th>Zn immersion</th>
<th>Acidic e.p.</th>
</tr>
</thead>
<tbody>
<tr>
<td>WE43</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZK31</td>
<td></td>
<td>x</td>
<td>x</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AZ31</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg pure</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Characterisation of the coatings**

Upon chemical pre-treatment, the appearance of the sample surfaces changes as shown in Fig. 2.5.1a; after pickling the surface is shiny and grain boundaries and precipitates are visible by OM and SEM (Fig. 2.5.1b and Fig. 2.5.3a). By the subsequent activation the samples are further etched and the surface partially loses its shininess. By immersion in the Zn-containing solution, the surface changes to a dark grey and blueish colour (Fig. 2.5.1a).

![Figure 2.5.1](image)

**Figure 2.5.1:** (a) Photograph of a polished, pickled, Zn-immersed and acidic electroplated surface, respectively; and (b) optical micrograph of a pickled sample.

In XRD measurements (Fig. 2.5.2) peaks for Mg and Mg$_{41}$Nd$_{3}$ (small and unlabelled peaks mainly in the 2θ range from approximately 30–40°) were detected for the pickled samples. After zinc immersion metallic Zn and Mg were present. By acidic electroplating, the Zn peak intensity increased, while the one of Mg decreased, indicating a thicker Zn layer.
The SEM images taken after the various steps of chemical pre-treatment are shown in Fig. 2.5.3. As described above the surface was slightly etched during pickling. The EDX measurements of areas within the grains revealed mainly the presence of Mg, but also some Y, O and P were found. By the activation process the surface became rough and grain boundaries were further etched. The elements Mg, Y, O and C were measured by EDX spectroscopy. The SEM analysis of Zn-immersed samples with varying immersion times (1, 3 and 10 min) indicates that even after 1 min of immersion a great part of the sample surface was covered by Zn (Fig. 2.5.3c). After 3 min hardly any substrate material (dark areas in Fig. 2.5.3f) was visible anymore. For

![Figure 2.5.2: XRD data of polished, pickled, Zn-immersed and acidically electroplated (e.p.) WE43.](image)

the Zn layers two different surface morphologies seem to exist (Fig. 2.5.3e); some areas were hilly and rough, while others were smooth and the grain boundaries of the Mg substrate were visible. EDX measurements on the grain boundaries revealed a reduced Zn content compared to the grain interior. At higher magnification at not completely Zn-covered sites (Fig. 2.5.3f), it can be seen that the hilly and rough areas were bound to the substrate, while the smooth ones grew on them. The EDX measurements of uncovered areas indicated signals for the elements Mg, Y and O. In general, after 3 min of zinc immersion only a few areas stayed Zn-free (Fig. 2.5.3e).
Their amount was further reduced by immersion for 10 min (Fig. 2.5.3g) or by re-activation followed by re-immersion after a first chemical pre-treatment (Fig. 2.5.3h). However, they could not be removed completely, which might cause problems during further electroplating.

Figure 2.5.3: SEM images of sample surfaces after the various pre-treatment steps; (a) after pickling; (b) after activation; (c and d) after 1 min of Zn immersion; (e and f) after 3 min of Zn immersion; (g) after 10 min of immersion; and (h) after re-activation and Zn re-immersion.
The cross-sections of Zn undercoats (Fig. 2.5.4a), however, appear homogeneous (also in the vicinity of precipitates) and seem to completely cover the surface. Cross-sections of acidic electroplated samples show generally a compact Zn layer with a relatively smooth outer surface (Fig. 2.5.4b). The interface between the substrate and the Zn coating was rough, leading to an interlocking of the layer and the substrate and thus improving the adhesion of the layer. However, some inhomogeneities in the shape of “bumps” were observed (Fig. 2.5.4c). Probably, they originated from the non-uniformity of the chemical Zn underlayer; at Zn-free sites the substrate material was exposed to the acidic electrolyte, it corroded leading to evolution of gaseous hydrogen and to inhomogeneous Zn deposition. The thicknesses of the electroplated Zn coatings were approximately 3–6 µm and 15–20 µm after 3 and 15 min acidic electroplating, respectively.

![Figure 2.5.4: SEM images (back scattered electrons) of cross-sections of (a) a Zn underlayer; (b) an acidic electroplated Zn layer (e.p. time: 3 min); and (c) an acidic electroplated Zn layer containing an inhomogeneity/“bump” (e.p. time: 10 min).](image)

In order to avoid inhomogeneities in the Zn coating due to corrosion of the Mg substrate in the acidic electroplating bath, electroplating in an alkaline electrolyte (pH: 13.7) prior to acidic electroplating was performed. Photographs of an alkaline and of a combined alkaline and acidic electroplated sample are shown in Fig. 2.5.5a and b. After 30 min of alkaline electroplating the surface appeared dark and was not very shiny. During the subsequent acidic electroplating (30 min) a greyish and shiny surface developed. In the SEM image of the cross-section of the latter sample (Fig. 2.5.5c) the difference between the substrate, the alkaline and the acidic Zn layer is clearly visible: the alkaline Zn layer is porous, but fewer inhomogeneities/“bumps” are observed.
compared to the “only” acidic Zn coating. The acidic Zn layer on it is dense and uniform. Thus alkaline electroplating seems to be a good base for further acidic electroplating.

Heat treatments at 300°C of the combined alkaline and acidic electroplated samples, which should improve the adhesive strength, led to blister formation under the coating even after short times, which in turn led to delamination of the Zn coating. As a consequence, heat treatments were considered to be unsuitable for alkaline electroplated specimens. To compare, in acidic electroplated samples the coating did not delaminate and a diffusion zone formed upon the heat treatment. But the surface turned dark, lost its shininess and pore-like microstructural defects in the outer part of the layer were observed.

![Figure 2.5.5: Photographs of (a) an alkaline (30 min) and (b) an alkaline and acidic electroplated Zn layer (e.p. time: 30 min each); and (c) SEM image of the cross-section of sample (b).](image)

**Characterisation of the degradation behaviour**

Results from immersion testing (Fig. 2.5.6a) indicate that the Zn electroplatings protected the material underneath at the very beginning (first 2 to 24 h); the Zn-coated samples evolved less hydrogen than their polished counterparts. However, soon local corrosion attacks started leading to galvanic corrosion and subsequently a drastic increase in hydrogen evolution. The time for break-down of the coating varied and depended on the thickness and the homogeneity of the coating. The acidic Zn layers (coating thickness: 3–6 and 15–20 μm, respectively) only lasted for a few hours (2–
4 h), while in the combined alkaline and acidic electroplated coatings (coating thickness: 20–25 μm) enhanced corrosion occurred after approximately 10–24 h. Generally, the samples with thicker coatings lasted longer. However, the quality of the coating was also very important. Despite being produced in the same way, i.e. alkaline and acidic electroplated (each for 30 min), samples d) and e) in Fig. 2.5.6 show large variations in hydrogen evolution with time; in sample d) local corrosion attacks at the edge were observed after 10 h of immersion in SBF, while in sample e) the surface seemed not heavily damaged after 24 h. However, care must be taken as in sample e) the non-coated area was cut off, while for sample d) it was only sealed. Possibly, corrosion occurred under the sealing and thus the measured hydrogen originated not only from the coating. It was also observed that the differently produced and corroded samples looked different; from the acidic Zn coatings large areas of the coatings were delaminated upon immersion in SBF (Fig. 2.5.6c), while in the combined Zn coatings spot-like local corrosion attacks occurred (Fig. 2.5.6d–e). Samples which were only chemically treated (Zn immersed), exhibited the lowest corrosion resistance (Fig. 2.5.6a, b); the Zn underlayer was not uniform and thus the Mg substrate got in contact with the electrolyte leading locally to galvanic corrosion and consequently massive hydrogen production.

![Figure 2.5.6](image-url)

**Figure 2.5.6:** (a) Time dependent hydrogen evolution of various Zn-coated WE43 samples. Photographs of corroded samples; (b) Zn-immersed sample, after 8 h in SBF; (c) acidic electroplated sample, after 8 h in SBF; (d, e) alkaline and acidic e.p. samples, after 24 h in SBF.
Discussion

Because of the high reactivity of Mg alloys, the chemical pre-treatment is the critical step in obtaining homogeneous, pore-free and uniform electroplatings, which are required when protecting a substrate by a nobler element. This is especially important when using an acidic electrolyte for plating, as at low pH values corrosion of the substrate occurs, which may generate inhomogeneities underneath the coating. However, the development of a suitable chemical pre-treatment is challenging, because among other factors it is alloy-dependent. For instance, the standard pre-treatment procedure suggested by ECHEM was not successful for WE43. Thus, a new chemical pre-treatment process had to be developed to this purpose.

During this study, it was found that pickling solutions based on phosphoric acid worked well with the chosen activation and zinc immersion procedure for both acidic and alkaline electroplating of WE43 samples. However, the pickling time needed to be kept relatively short (i.e. 30 s); long-lasting pickling led to local corrosion attacks, which could not be overcome or removed by activation and/or zinc immersion and which impaired the Zn coverage of the underlayer. After electroplating, a rough interface between the substrate and the Zn coating was noted. This is advantageous as the adhesion of the layers can be improved by mechanical interlocking. It is assumed that this rough interface originates mainly from activation. By pickling the surface is etched and slightly roughened, but not all oxides were removed as the presence of oxygen in EDX measurements revealed. During activation the grain boundaries and the grain interiors were further attacked leading to a rough surface, on which the Zn underlayer formed.

Analysis of the Zn underlayers by SEM (Fig. 2.5.3) indicates that Zn deposition occurs basically in two stages. Firstly, “insular” Zn deposition took place on the activated substrate surface. With time, these “islands” grew and touched each other. Secondly, Zn crystals of approximately 0.25–1 μm in size formed on the first Zn layer. According to [56] Zn deposition occurs by the reaction $\text{Mg} + \text{Zn}^{2+} \rightarrow \text{Mg}^{2+} + \text{Zn}$ and starts at cathodic sites, such as precipitates or grain boundaries. Similar to [61], where after 30 s of zinc immersion a Zn surface coverage of 80% was reached, our samples
also exhibited Zn deposition quickly. An explanation for the fast initial Zn deposition is that at the beginning only little hydroxide is present on the Mg surface. The Zn layer forms rapidly on the cathodic sites of the substrate [56, 61], such as the precipitates, which were not detectable by SEM anymore after zinc immersion. Moreover, it has been published that residual hydroxides can react with the pyrophosphate from the solution to form soluble complexes, and lead to exposure of Mg to the electrolyte and Zn deposition at cathodic sites [61]. With immersion time hydroxide forms due to dissolution of the Mg surface. However, because this hydroxide is not very dense, Zn ions can diffuse through it and form a new, slow-growing Zn layer [56, 61]. Unfortunately, in all samples Zn-free areas were also observed. To avoid such Zn-free areas, firstly, the immersion time was prolonged to 10 min; secondly, the chemically pre-treated samples were re-activated and re-immersed in the zinc immersion solution. In the latter procedure, loose Zn layers from the first chemical pre-treatment were removed and then replaced by a new Zn layer. However, it was not possible to completely cover the Mg substrate surface by Zn, but compared to similar Zn undercoats from literature [53] our layers appeared more compact and dense. The Zn-free areas are a major issue during electroplating. Magnesium in contact with Zn is exposed to the environment (i.e. electroplating bath) causing corrosion of the substrate and hydrogen evolution leading to spots underneath the coating. Despite being covered by Zn, such “bumps” are defects in the layer, where adhesion is insufficient and which are more prone to corrosion. Consequently, the material underneath is insufficiently protected, and moreover, enhanced corrosion can take place, as has been shown by immersing the samples in SBF. Such local corrosion attacks under Zn electroplatings were also published elsewhere [62].

To overcome this issue, electroplating in an alkaline bath prior to acidic electroplating was performed, because at pH values above 11 Mg is immune, according to the Pourbaix diagram [63]. Alkaline electroplated layers indeed featured fewer inhomogeneities. Defect-free layers were still not achieved, however, and they were also porous. But, alkaline Zn coatings served as good base for further acidic electroplating; the acidic layers produced on them appeared compact and dense. The
improvement of adhesive strength of such combined coatings by heat treatments at 300°C was not successful, however; all heat treatments, independent of their duration and temperature, led to delamination of the coating. The gas and possibly also liquid entrapped in the pores of the alkaline layer expanded at elevated temperature, blisters formed under the coating and the layer was separated. It was reported that porous platings can develop due to hydrogen gas at the surface, which arise from a change of bath composition or insufficient wetting [57]. However, as for each sample fresh electrolyte was used, a change in bath composition can be excluded. Problems with remelting of combined alkaline and acidicly electroplated Zn coatings were also encountered by other researchers [64]. In order to avoid delamination of the Zn coating some strategies were employed; alkaline plating was kept brief to produce only a thin Zn layer, short heating times (5 min) and lower temperatures (200°C) were investigated and the bath composition was slightly changed. In summary, however, it was not possible to reduce the porosity and improve the adhesive strength of alkaline electroplated coatings by heat treatments. In acidic electroplated samples, on the other hand, heat treatments led to diffusion of Zn into the substrate, but at the same time also to a decrease in the quality of the outer Zn layer. So far no homogeneous and uniform Zn coatings could be electroplated on the Mg alloy WE43. But it can be assumed that the adhesive strength of acidic electroplated samples, which feature fewer defects, can be improved by heat treatments.

Corrosion tests of electroplated WE43 specimens in SBF indicated that the Zn coatings produced provided some protection at the very beginning of immersion. Often during the first day of immersion, local corrosion attacks started and the protective ability of the coating was destroyed. Generally, combined alkaline and acidic electroplated samples performed better than their acidic counterparts. However, the time for the coating’s break-down varied a lot between the variously treated samples and also between the samples coated in the same way. This is ascribed to the generation of local inhomogeneities during electroplating, which offer sites for local corrosion to initiate. In addition, it is possible that the sealing of the non-coated areas was not completely tight, leading also to corrosion and hydrogen evolution from these
areas. To avoid possible contact between the non-coated area and the electrolyte, electrochemical impedance spectroscopy (EIS) measurements over a period of 24 h were performed (measured every 2 h at the open circuit potential (OCP)) on a 1 cm² large surface area. However, due to local (crevice) corrosion at the edge of the sealing during the first measurement, it was not possible to analyse the performance of the coating. But, from the OCP values, which decrease with time from approximately -1.0 V (vs. SCE) being close to the OCP of Zn, to -1.3 V (vs. SCE) moving towards the OCP of Mg, it can be stated that at the beginning the electrolyte sees a Mg-free Zn layer. Similar results were obtained in [62]. There, the Zn coatings did not provide sufficient protection over a long time period as well; after 18 h in a 0.15 M NaCl solution the corrosion potential decreased from a value close to that of pure Zn to a value close to the one of the substrate material, while the corrosion current increased [62]. However, no information was given on how the samples corroded.

In summary, to achieve improved corrosion resistance high-quality Zn coatings with good adhesion and uniformity must be produced. So far, combined alkaline and acidic electroplated Zn layers exhibited the “best” corrosion resistance among the tested samples. However, their performance is not good enough to use such coated Mg alloy as implant substrate material.

Conclusions

In this study a chemical pre-treatment prior to electroplating was elaborated for the Mg alloy WE43, where a relatively dense and compact metallic Zn underlayer was deposited on the surface, which reduced the reactivity of the substrate and made a subsequent acidic or alkaline electroplating possible. Among various pickling solutions it turned out that solutions based on phosphoric acid are the most suitable for WE43.

The quality of the Zn underlayer is a very important issue for the success of the subsequent electroplating process, especially in the acidic bath. However, the Zn underlayers produced exhibited some Zn-free areas, which led to the formation of “bump”-like inhomogeneities during acidic electroplating, due to corrosion of Mg
exposed to the electrolyte and the hydrogen gas related to it. Such inhomogeneities have a negative influence on the degradation performance; local corrosion attacks can start at these damaged areas after a few hours of immersion in SBF. Consequently, the layer breaks and galvanic corrosion occurs. By electroplating in an alkaline bath prior to acidic electroplating, the defect density was reduced and the degradation resistance in SBF slightly increased. However, local corrosion attacks followed by galvanic corrosion started after approximately 1 day of immersion.

In order to improve the adhesive strength of the coating, heat treatments at 300°C were performed to induce diffusion of Zn. In Zn coatings formed from an acidic bath, a diffusion zone was observed, but it seemed that the outer surface of the coating partially lost its smoothness. Alkaline electroplated Zn coatings delaminated during the heat treatment due to their porosity.

In conclusion, to improve the corrosion resistance of the Mg alloy WE43 by electroplating of Zn, a defect-free coating must be produced. In this work, protection of the substrate material was achieved during the first day of immersion. However, to be suitable for osteosynthesis the quality of the Zn coating needs be improved. In addition, due to the increased corrosion rate that develops once the coating is penetrated, the application of Zn coatings is not the most promising strategy.
2.6 References

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Chapter 3

Alloy development

In the first part of this chapter, the reduction of the hot tearing susceptibility of Mg–Zn alloys by the addition of Y or Yb, which was discovered during direct chill casting of test alloys, is explained by means of further experiments and thermodynamic calculations. These findings are not only important for processing of Mg alloys for osteosynthesis, but they also have a great impact on direct chill casting of Mg alloys in general. In chapter 3.2, new high-strength Mg alloys are presented. Thereby, the design strategy, which aims at grain-refinement during the course of production, the attractive mechanical properties (i.e. high strength at moderate ductility) and the influence of heat treatments and the microstructure on the mechanical properties are elucidated.
3.1 Influence of the addition of Y and Yb on the hot tearing susceptibility of Mg–Zn alloys

Introduction

Hot tearing (HT), also known as hot cracking, hot shortness or hot brittleness, is a major defect which can arise during solidification. It is defined as failure occurring in the mushy zone of a freezing alloy, i.e. at solid fraction \( f_s < 1 \). Numerous publications as well as industrial experience regarding the hot tearing phenomenon show that HT occurs in the terminal stages of solidification when the solid fraction exceeds 0.85 to 0.95. According to Eskin et al. [1] four stages of solidification characterise the permeability of the solid network: (i) mass feeding, where the liquid and the solid can freely move; (ii) interdendritic feeding, where the dendrites start to form a solid network and the liquid must flow through the network; (iii) interdendritic separation, where the liquid network becomes fragmented; and (iv) interdendritic bridging, where the structure develops moderate strength. The last two stages are important for the occurrence of HT. Here, with increasing solid fraction, the permeability of the solid network becomes very low and liquid feeding ceases. Because thermal contraction occurs simultaneously, strains may develop. If the strain (and the strain rate) imposed on the solid network is greater than a critical value, hot cracking occurs. Thus, it is mainly during the 3rd stage, i.e. interdendritic separation, that the structure is vulnerable to HT. However, the extent to which this happens depends strongly on the temperature dependence of the volume fraction \( f_s \) in the temperature range at the terminal period of solidification, \( f_s(T) \) for \( f_s > 0.9 \). According to Djurdjevic and Schmid-Fetzer [2] this partial freezing range near termination of solidification, or “terminal freezing range” (TFR), may be taken as the freezing range from 90 to 98% solid fraction, \( \Delta T_{90/98} \). It indicates the TFR of the “almost” last 10% of the solidifying.

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1 See also P. Gunde, A. Schiff, P.J. Uggowitzer, Materials Science and Engineering A 527 (2010) 7074-7079.
liquid. This value is assumed to be more relevant than $\Delta T_{90/100}$ because at $t_s \geq 0.98$ the structure develops considerable strength and solid-state creep can compensate the strain caused by thermal contraction [3]. Since the degree of thermal contraction is proportional to the TFR and here the structure is susceptible to HT, it seems reasonable to view the TFR as a rough measure of an alloy’s hot tearing susceptibility (HTS). With regard to the HTS of Mg alloys, various papers describe the effect of the respective chemical composition and relate it partly to the solidification path at the end of solidification [4] and to the time period where the solidifying alloy is vulnerable to HT [5-10], which in turn correspond approximately to the TFR.

In the course of producing Mg–Zn–Ca(–Y) [11-13] and Mg–Zn–Zr–Ca–Yb alloys (see section 3.2) via the direct chill casting route, we observed a remarkable influence of the Y and Yb content, on the alloy’s HTS. Even small Y additions to Mg alloys containing 2–3 wt.% Zn resulted in a significant reduction of the HTS. In the first part of this chapter this effect is investigated in more detail by comparing the HTS with the TFR of Mg-3Zn-Y alloys with systematically varied Y content. The purpose is to examine the HTS of these alloys in permanent mould and direct chill casting, and to correlate it to the specific TFR. By analysis of the experimental data and by performing thermodynamic calculations, the improvement of HTS by the addition of Y is explained in detail. In the second part, the positive influence of Yb on HTS is addressed. It is discussed based on experimental data and the learning from the addition of Y. No thermodynamic calculations could be performed, however, as the element Yb is not (yet) available in the database used.

Experimental

Casting experiments – permanent mould and direct chill casting

The evaluation of the HTS of Mg-3Zn-Y alloys was carried out by means of industry-relevant casting experiments. The first experiment was performed using a permanent star-shaped steel mould (PSM), similar to that described in [1]. The geometry of the cast component is shown in Fig. 3.1.1. The rod length variations (head to head
distance) were as follows: 25, 45, 65, 95, 125 and 175 mm; all were 10 mm in diameter. The rods’ dog-bone shape prevented free contraction during solidification. For each alloy composition, five casting trials were performed. Prior to each 5-trial series the mould was coated with BN. For all casting experiments the mould was preheated to a temperature of 250±5°C. Independent of the alloys’ chemical composition, the pouring temperature was 700±5°C. As shown below, the liquidus temperature of all alloys was about 640°C, i.e. the superheat was approximately 60°C. The average cooling rate in the temperature range between 600°C and 300°C was about 30 K s⁻¹. The mould was opened approximately 5 min after pouring, and the castings were examined for cracks with the naked eye and using a 10x magnifying glass.

The second experiment was a direct chill casting (DCC) process. Billets were produced at LKR using a MAGNUMCAST automated casting machine with hot-top technology [14]. The melt was heated to 700±5°C in an electric furnace with a capacity of 600 kg. A protective gas mixture of 1.5% HFC134a and N₂ was deployed. Cylindrical billets of 152 mm in diameter and an average length of 1800 mm were cast, at a cooling rate of about 10 K s⁻¹. For each alloy composition one billet was produced and inspected.

For both the PSM and the DCC experiments, Mg alloys with the following nominal chemical composition were used (in wt.%): Mg-3Zn-0.5Zr, Mg-3Zn-0.5Zr-0.4Y, and Mg-3Zn-0.5Zr-0.8Y. The exact chemical compositions of the components produced, measured by spark source optical emission spectroscopy, are given in Table 3.1.1. Zirconium was added for grain refinement and its amount was kept constant for
all alloys. In this study it will not be considered as an element influencing HTS, and will for reasons of clarity not be incorporated into the thermodynamic calculations.

Table 3.1.1: Chemical compositions (alloying elements in wt.%; Mg remainder) of the PSM rods (average of five trials) and DCC billets (average of two trials).

<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>PSM</th>
<th>DCC</th>
<th>PSM</th>
<th>DCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-3Zn-0.5Zr</td>
<td>3.17±0.05</td>
<td>0.54±0.03</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Mg-3Zn-0.5Zr-0.4Y</td>
<td>2.94±0.02</td>
<td>0.43±0.04</td>
<td>0.43±0.05</td>
<td>–</td>
</tr>
<tr>
<td>Mg-3Zn-0.5Zr-0.8Y</td>
<td>3.20±0.03</td>
<td>0.47±0.03</td>
<td>0.79±0.04</td>
<td>0.67±0.01</td>
</tr>
</tbody>
</table>

Characterisation

The microstructures of all samples were investigated using optical microscopy (OM) and scanning electron microscopy in the backscattered electron mode (BSE SEM; Hitachi SU-70, operated at 15 kV). For phase identification two techniques were employed: X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX). XRD measurements were conducted using a PANalytical X’Pert PRO-MPD diffractometer (Cu Kα1 source operated at 37 kV and 45 mA); EDX measurements (Oxford Instruments) were performed at 5 kV. The volume fraction of the intermetallic phases (IMP) was determined by means of optical analysis of OM images (analySIS FIVE–Digital Imaging Solutions) and of BSE SEM images (ImageJ) image processing [15]. The solidus temperatures were measured by means of differential scanning calorimetry (DSC 220CU, Seiko Instruments) operated at a heating rate of 20 K min⁻¹ under a constant Ar flow of 50 ml min⁻¹. Thermodynamic calculations were performed using the simulation software tool PANDAT with the PanMg8 database [16].

Results

The PSM castings were examined optically and a number representing the hot tearing susceptibility (HTS委宣传) was allocated to each alloy. This number was obtained by examining each rod and assigning a value between 0 and 1 according to the following
scheme: 1 for completely broken rods; 0.5 for obviously cracked rods; 0.25 for rods with cracks detectable only with the magnifying glass; and 0 if no cracks were observed. The final HTS\textsubscript{PSM} represents the average value of the sum of the six rods of all five trials (note: HTS\textsubscript{PSM}=6 is the theoretical upper limit if all six rods are completely broken, while HTS\textsubscript{PSM}=0 represents the “best case” if the alloy is not susceptible to HT under the given casting conditions).

The DCC billets were cut into four segments at positions of 1000 and 1300 mm from the bottom of the billets. The cross-sections of the segments were metallographically prepared (ground) and examined optically for hot cracks. Since the alloys show only surface cracks but no evidence of centre cracks, and since the average crack length (a\textsubscript{c}) is of the same order of magnitude for all alloys and trials (a\textsubscript{c}=11.3±2.8 mm, 12.9±1.6 mm, 9.8±1.2 mm for Mg-3Zn-0.5Zr, Mg-3Zn-0.5Zr-0.4Y and Mg-3Zn-0.5Zr-0.8Y, respectively) the average number of surface cracks was chosen as a measure of the alloy’s hot tearing susceptibility (HTS\textsubscript{DCC}).

![Figure 3.1.2: Hot tearing susceptibility evaluated by means of (a) permanent star-shaped mould casting (HTS\textsubscript{PSM}) and (b) direct chill casting (HTS\textsubscript{DCC}).](image)

Figure 3.1.2 shows the ranking of the alloys according to their hot tearing susceptibility, HTS\textsubscript{PSM} and HTS\textsubscript{DCC}. It is obvious that the Y content significantly influences the alloy’s solidification performance. Even a slight increase in Y additions results in reduced hot cracking. Although HTS\textsubscript{PSM} and HTS\textsubscript{DCC} reflect susceptibility only from a qualitative point of view, the advantage of adding Y seems to be more significant in the DCC experiment.
Discussion

Effect of Y addition on HTS

Clyne and Davies [17] proposed a cracking susceptibility coefficient (CSC) for the estimation of compositional effects on the HT vulnerability of alloys, defined as:

$$\text{CSC} = \frac{t_y}{t_R}$$  \hspace{1cm} (3.1)

where $t_y$ is the period during solidification during which the alloy is “vulnerable” to hot cracking, and $t_R$ is the time available for stress relief processes. The numerator $t_y$ corresponds to the period of interdendritic separation during which the liquid phase becomes fragmented and feeding ceases. It was suggested as being the time period for the fraction between 90 and 98% solid fraction (in contrast to [17], 98% rather than 99% was chosen; see Introduction of chapter 3.1). The denominator $t_R$ corresponds to the period of interdendritic feeding during which the dendrites start to form a solid network, supposed to be the period where the solid fraction increases from 40 to 90%. Thus CSC can be written as:

$$\text{CSC} = \frac{t_{0.98} - t_{0.9}}{t_{0.9} - t_{0.4}}$$  \hspace{1cm} (3.2)

Let us now consider the situation in the Mg-3Zn-Y system. Thermodynamic calculations reveal that an increase in Y changes the latent heat ($L$) of the alloys to a very small extent, from 8.27 kJ mol$^{-1}$ (0 wt.% Y) to 8.46 kJ mol$^{-1}$ (0.8 wt.% Y). In addition, the cooling curves ($L$ vs. $T$) calculated according to Scheil solidification are more or less identical, in the range $0<L<0.9$ L for all alloys. Thus, since the heat release $dQ/dt$ can be assumed to be identical for all alloys in the PSM and DCC experiments, Eq. 3.2 can be modified to:

$$\text{CSC} = \frac{\Delta L (T_{0.9} - T_{0.98})}{t_{0.9} - t_{0.4}}$$  \hspace{1cm} (3.3)
with A as conversion factor. In addition, for both the PSM and DCC experiments the denominator in Eq. 3.2 \( (t_{0.9} - t_{0.4}) \) can be assumed to be constant and Eq. 3.3 results in:

\[
\text{CSC}^* = T_{0.9} - T_{0.98} = \text{TFR} \tag{3.4}
\]

Therefore, in a first approximation, an alloy’s susceptibility to hot tearing should be reflected by its terminal freezing range. This statement, however, is only valid under the same casting conditions and comparable cooling curves \( L(T) \) in the range \( 0 < L < 0.9 \) L. With regard to the PSM and DCC experiments one must keep in mind that their cooling rates are different: approximately \( 30 \text{ K s}^{-1} \) for PSM and approximately \( 10 \text{ K s}^{-1} \) for DCC. Thus the term \( (t_{0.9} - t_{0.4}) \) will differ for PSM and DCC, and a direct comparison of the respective CSC values is not appropriate.

The question is now how the TFR can be determined for particular alloy compositions. Figure 3.1.3 shows the terminal section of the “solid fraction vs. temperature” \( f_s(T) \) curve in the range of \( 0.8 < f_s < 1 \) for the three alloys, calculated according to the lever rule (equilibrium) and Scheil (non-equilibrium), respectively. It is clear that the solidification mode, “Lever” or “Scheil”, has a great influence on the \( T_{0.9} - T_{0.98} \) value: the TFR is much larger for non-equilibrium than for equilibrium. However, the TFR values do not vary systematically (see Table 3.1.2); in fact, they decrease monotonically only for the “Lever” mode. Consequently, the simplified view via “Lever” or “Scheil” cannot explain the HTS results shown in Fig. 3.1.2, and a

![Graph showing solid fraction vs. temperature for the binary Mg-3Zn alloy and for alloys with 0.4 wt.% and 0.8 wt.% yttrium, calculated for equilibrium (Lever) and non-equilibrium (Scheil).](image-url)

Figure 3.1.3: Solid fraction vs. temperature for the binary Mg-3Zn alloy and for alloys with 0.4 wt.% and 0.8 wt.% yttrium, calculated for equilibrium (Lever) and non-equilibrium (Scheil).
Table 3.1.2: Characteristic temperatures and terminal freezing range (TFR) in (°C); TL: liquidus temperature, TS: solidus temperature, T_{0.9}: temperature at f_s=0.9, TFR=T_{0.9}-T_{0.98}.

<table>
<thead>
<tr>
<th></th>
<th>Mg-3Zn</th>
<th>Mg-3Zn-0.4Y</th>
<th>Mg-3Zn-0.8Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>TL</td>
<td>641</td>
<td>640</td>
<td>639.5</td>
</tr>
<tr>
<td>T_{S/Lever}</td>
<td>537</td>
<td>560</td>
<td>576</td>
</tr>
<tr>
<td>T_{0.98/Lever}</td>
<td>557</td>
<td>570</td>
<td>580</td>
</tr>
<tr>
<td>TS/Scheil</td>
<td>341</td>
<td>341</td>
<td>341</td>
</tr>
<tr>
<td>T_{0.98/Scheil}</td>
<td>341</td>
<td>341</td>
<td>460</td>
</tr>
<tr>
<td>T_{S/PSM}</td>
<td>341±3</td>
<td>460±5</td>
<td>530±3</td>
</tr>
<tr>
<td>T_{S/DCC}</td>
<td>341±3</td>
<td>470±3</td>
<td>530±3</td>
</tr>
<tr>
<td>T_{0.9/Lever}</td>
<td>598</td>
<td>594</td>
<td>589</td>
</tr>
<tr>
<td>T_{0.9/Scheil}</td>
<td>570</td>
<td>573</td>
<td>579</td>
</tr>
<tr>
<td>TFR_{Lever}</td>
<td>41</td>
<td>24</td>
<td>9</td>
</tr>
<tr>
<td>TFR_{Scheil}</td>
<td>229</td>
<td>232</td>
<td>119</td>
</tr>
</tbody>
</table>
| TFR_{PSM} | 257±3\_\text{Lever} & 134±5\_\text{Lever} & 59±3\_\text{Lever} &  
  229±3\_\text{Scheil} & 113±5\_\text{Scheil} & 49±3\_\text{Scheil} &  
| TFR_{DCC} | 257±3\_\text{Lever} & 124±3\_\text{Lever} & 59±3\_\text{Lever} &  
  229±3\_\text{Scheil} & 103±3\_\text{Scheil} & 49±3\_\text{Scheil} &  

PSM: permanent star-shaped mould; DCC: direct chill casting  
* calculated with \(T_{0.9/Lever}\)  ** calculated with \(T_{0.9/Scheil}\)

more detailed consideration of the solidification mode is required. In the following the “real” mode is illustrated on the basis of selected characteristics: microstructural features (i.e. type and amount of intermetallic phases); and the measured solidus temperature. Figure 3.1.4 shows the microstructure of the various alloys, and Table 3.1.3 summarises the data calculated and measured for the intermetallics present in the PSM- and DCC-processed alloys (note: due to the complexity of the Mg–Zn–Y system and the low content of the intermetallic phases their identification by means of XRD and EDX is incomplete; the experimental data listed in Table 3.1.3 is not representative of the real situation but reflects real trends). Various peculiarities can be noted: (i) all microstructures exhibit a noticeable amount of intermetallic phases (white areas in Fig. 3.1.4); (ii) the type and amount of intermetallic phases differ significantly from calculations by means of Pandat for both “Lever” and “Scheil” solidification (for “Lever” the IMP content increases to 0.82 vol.% with increasing Y, while for “Scheil” the overall amount decreases from 2.9 to 2.0 vol.%; for PSM and DCC the IMP fraction is between “Lever” and “Scheil”, but closer to “Scheil”); (iii) the amount of
intermetallic phases is slightly lower in DCC than in PSM alloys; (iv) within one experiment series the grain size decreases marginally with increasing Y content and is lower in PSM than in DCC alloys (PSM: 31 to 26 μm; DCC: 43 to 38 μm). From these observations the following conclusions can be drawn: (i) and (ii) the solidification mode is somewhere between “Lever” and “Scheil”; (iii) with higher IMP content PSM solidification is a bit closer to “Scheil”, which can be explained by the higher cooling rate; (iv) Y slightly increases the “grain growth restriction factor” [13, 18], leading to a reduced grain size, and the higher cooling rate during PSM results in a smaller grain size. Although it is well known that grain refinement usually has a positive effect on
HTS, the slight grain size variation within one casting series will probably not influence HTS, especially in view of the globular grain morphology [19].

Table 3.1.3: Calculated and measured IMP type and volume fraction formed during solidification.

<table>
<thead>
<tr>
<th></th>
<th>Mg-3Zn</th>
<th>Mg-3Zn-0.4Y</th>
<th>Mg-3Zn-0.8Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lever</td>
<td>–</td>
<td>MgYZn₃ (0.47%)</td>
<td>MgYZn₃ (0.82%)</td>
</tr>
<tr>
<td>Scheil</td>
<td>MgZn₃ (2.9%)</td>
<td>MgZn₃ (2.1%)</td>
<td>MgZn₃ (1.3%)</td>
</tr>
<tr>
<td></td>
<td>MgYZn₃ (0.4%)</td>
<td></td>
<td>MgYZn₃ (0.7%)</td>
</tr>
<tr>
<td>Exp. PSM</td>
<td>MgZn₃ (1.1±0.2%)</td>
<td>Mg₃YZn₆ (1.9±0.3%)</td>
<td>Mg₃YZn₆ (2.0±0.3%)</td>
</tr>
<tr>
<td>Exp. DCC</td>
<td>MgZn₃ (0.9±0.2%)</td>
<td>Mg₃YZn₆ (1.8±0.3%)</td>
<td>Mg₃YZn₆ (1.8±0.3%)</td>
</tr>
</tbody>
</table>

In order to quantitatively classify the “real” solidification mode, the solidus temperature was determined by means of DSC. Figure 3.1.5 illustrates the experimental results, compared to calculated $T_s$ and $T_{0.98}$ values for equilibrium and Scheil solidification in dependence on the Y content. As expected from Fig. 3.1.3 the solidus temperature for equilibrium solidification is generally high, and increases somewhat with increasing Y content. On the other hand, $T_s$ in the case of Scheil solidification remains at a very low level – the temperature is at 341°C identical to the eutectic temperature of the binary Mg–Zn system. At about 2.5 wt.% Y, however, a sharp increase can be observed. The picture changes significantly if $T_s$ is replaced by
The temperature increase shifts to a much lower Y content of about 0.5 wt.%. The reason for this significant difference between $T_s$ and $T_{0.98}$ lies in the flat slope of the $f_s(T)$ curve at the end of solidification with simultaneously small eutectic fraction. As can be seen in Fig. 3.1.3 all alloys exhibit the same $T_s$ value, but the dotted horizontal line for $f_s=0.98$ intersects the Scheil curve for 0.8 wt.% Y at 460°C. For the alloys with lower Y content the eutectic content is above 2 vol.%, which results in identical $T_s$ and $T_{0.98}$ values. This peculiarity needs to be discussed in more detail with respect to the measured $T_s$ data, because it may be considered as a weak point in the TFR concept. As shown in Table 3.1.3 and Fig. 3.1.4, the experimental alloys exhibit only a very low IMP content. This points to a low liquid fraction that eutectically transformed when the solidification terminated. Although DSC measurements allow determination of the solidus temperature even at low eutectic fractions, a reliable experimental determination of $T_{0.98}$ is not possible. Furthermore, if a final eutectic transformation and simultaneous flat $f_s(T)$ behaviour are absent, even the experimental determination of $T_s$ values seems to be unreliable. Nevertheless, in this study the DSC data for $T_s$ were taken for the determination of the TFR. As shown in Fig. 3.1.5 these data are positioned between $T_{0.98/Lever}$ and $T_{0.98/Scheil}$, which again indicates the particular solidification path. For 0.4 wt.% Y the $T_s$ value for DCC is slightly higher than for PSM, probably because of the lower cooling rate and thus somewhat closer-to-equilibrium solidification.

Table 3.1.2 summarises the data for $T_{s/PSM}$ and $T_{s/DCC}$ as well as the calculated $T_{0.9}$ data, from which the TFR values can be calculated according to Eq. 3.4, if $T_{0.98}$ is substituted by $T_s$. Since $T_{0.9}$ is slightly different for “Lever” and “Scheil”, different values are given for TFR$_{PSM}$ and TFR$_{DCC}$, respectively. Figure 3.1.6 illustrates in example form the dependence of the HTS of DCC casting on TFR. A good correlation between these figures is seen.

Even though the results given in Fig. 3.1.2 only reflect a qualitative ranking, the hot tearing susceptibility seems to be more pronounced for the PSM castings. There are at least two good reasons for this: firstly, the higher cooling rate shifts the solidification path further towards non-equilibrium and thus to lower solidus
temperatures (see $T_s$ data for 0.4 wt.% Y in Fig. 3.1.5) and higher TFR, respectively; and secondly, in Eq. 3.3 the denominator $(t_{0.9} - t_{0.4})$ is smaller for the PSM experiment and thus the CSC increases.

![Figure 3.1.6: Hot tearing susceptibility in direct chill casting (HTS$_{DCC}$) represented as a function of the terminal freezing range (TFR).](image)

The open question remains as to the metal-physical effect of the Y content on the TFR and in consequence on HTS. It can be seen from Table 3.1.3 that when Y is added, ternary intermetallics form. Obviously their existence is connected to an increase in measured solidus temperature. However, because the alloys solidify in non-equilibrium one cannot track their status in a pseudo-binary (Mg-3Zn)-Y phase diagram in order to locate the solidus temperature (note: the lack of a relevant database does not allow DICTRA simulations of the segregation during solidification). It may still be useful, though, to apply the following trick. It is known that non-equilibrium solidification generally leads to a quasi-reduction of the solidus temperature and thus to a shift of the tie-lines (change of the lever sections), associated with the formation of “unexpected” phases. Therefore it might be appropriate to shift the alloy’s status point to a somewhat higher Zn content in order to “see” these unexpected phases also in the equilibrium phase diagram. For example, increasing the Zn content from 3 to 8 wt.% produces the pseudo-binary phase diagram shown in Fig. 3.1.7. It essentially reflects the situation that may arise when Zn and Y are enriched in the liquid phase. Even if this “virtual” alloy with enrichment in
Zn and Y is not entirely correct, it helps us to understand the effect of Y. In the phase diagram all sections with liquid phase are shown in red. The solidus temperature clearly increases with increasing Y content due to the formation of Mg₃YZn₆. This phase was found in all microstructures of Y-containing alloys. In Fig. 3.1.7 the liquidus temperature for the Y-free alloy is the binary eutectic temperature (341°C); with increasing Y content the calculated \( T_s \) values increase. For alloys with \( Y > 1.5 \) wt.% the solidus temperature is equal to the temperature of the peritectic reaction liquid + MgYZn₃ \( \rightarrow \) Mg₃YZn₆. The calculated peritectic temperature is, at 543°C, very close to the measured \( T_s \) values (530°C) of the alloys with 0.8 wt.% Y. Accordingly, one can assume the position of the state point of the virtual alloy to be at \( Y > 1.5 \) wt.%, corresponding to an enrichment factor >1.9 (>1.5/0.8). The measured \( T_s \) values for the alloys with 0.4 wt.% Y (460°C; 470°C) lie on the phase boundary at a position of about 0.75 wt.% Y, corresponding to an enrichment factor of about 1.9 (0.75/0.4). Interestingly, the enrichment in Zn in the virtual alloys from 3 to 8 wt.% and in Y from 0.4 to 0.8 wt.% and 0.8 to >1.5 wt.%, respectively, to a certain extent reflects the more distinct element partitioning of Zn (\( k_{Zn} = 0.12 \)) compared to Y (\( k_{Zn} = 0.5 \)) [20].

![Figure 3.1.7: Pseudo-binary phase diagram for Mg-8Zn-Y.](image-url)
Effect of Zn on HTS

On the basis of Fig. 3.1.7 it is useful to discuss the possible influence of the Zn content on the HTS of Mg–Zn–Y alloys. Via the virtual element enrichment approach one can easily conclude that an increase in the Y/Zn proportion may result in reduced HTS. Alloys with reduced Zn content, e.g. types ZW21 and WZ21 [13], feature an increased Y/Zn ratio. Due to the reduced Zn content, the peritectic point shifts to a lower Y concentration; in the virtual system Mg-5Zn-Y, for instance, the peritectic point is at 0.6 wt.% Y, and the TFR can be assumed to be low even in alloys with relatively low Y content. Indeed, the casting experience of Light Metals Technologies (LKR) in Ranshofen, Austria, confirms this expectation of reduced HTS. In contrast to Y-free Zn-rich alloys of type ZK60, the ZW21 and WZ21 family shows no noticeable hot cracking behaviour.

Effect of Yb on HTS

In the course of this thesis, novel Mg–Zn–Yb–Zr–Ca alloys, which are presented in chapter 3.2 in more detail, were developed. During direct chill casting of the alloys, a positive influence of the element Yb on HTS was observed: during DCC of Mg-5Zn-2Yb-0.5Zr-0.25Ca alloys the HTS was significantly reduced compared to the Yb-free alloy, and no hot cracks were observed in the cast billet. The terminal solidification was characterised by the formation of a ternary Yb-containing intermetallic phase, as indicated by SEM and EDX. As a result the solidus temperature, estimated by DSC, increased from 295°C for the Yb-free alloy to approximately 390°C with the addition of Yb and consequently the TFR decreased. Thus, during DCC the TFR and the HTS are not only reduced by the addition of Y, but also by adding Yb.

Inspired by these results, new casting trials using the permanent star-shaped mould described above were performed and a series of Mg-3Zn-0.5Zr alloys with varying Yb content (0.2, 0.4, 0.8 and 2 wt.%) were produced and evaluated. Analysis of the PSM-cast rods featured improvement of rod quality and HTS when adding approximately 2 wt.% Yb to the alloy. However, the effect was not as significant as
with the addition of Y. The solidus temperature of the alloys estimated by DSC was approximately 400°C for all Yb-containing alloys. Thus in comparison with the Yb-free alloy the TFR is reduced, but it is larger compared to the Y-containing alloys. This can be a reason for the Yb’s less pronounced influence on the HTS during PSM casting. However, due to the different cooling rates in the PSM and DCC process and therefore different solidification, the minimum amount of Yb required for the improvement of HTS should be evaluated in further DCC trials.

**Conclusions**

It has been shown that adding Y and Yb has a very positive effect on the hot cracking of Mg–Zn–Zr alloys. In permanent mould castings as well as direct chill cast billets, alloying of few wt.% Y results in significant reduction of hot tearing susceptibility (HTS). The addition of Yb significantly reduced the HTS during DCC, while its effect was not that pronounced in PSM casting. The reduced HTS is attributed to the effect of Y and Yb on the solidification path at the terminal period of solidification where the permeability of the solid network becomes very low and liquid feeding ceases. Adding Y and Yb generates an increase in the solidus temperature of the multi-component system, shortening the terminal solidification path and reducing the terminal freezing range. The increase in the solidus temperature can be explained via a simple “virtual element enrichment” approach: it is caused by the formation of the ternary phase Mg$_3$YZn$_6$. A low Zn content also facilitates the Mg$_3$YZn$_6$ phase and thus reduces HTS. In the Yb-containing alloys, a ternary Mg–Zn–Yb IMP was found.

A simplified version of Clyne and Davies’ CSC model was used to illustrate the clear influence of the TFR on HTS, and to explain the alloys’ differing hot tearing behaviour in permanent mould and direct chill casting.

On the basis of the TFR concept a general rule may apply: HTS can be reduced by adding alloying elements (even in “homeopathic dosages”) which shorten the solidification path by facilitating terminal eutectic or peritectic transformation. Y and Yb perform this function, but other elements may also do the same.
3.2 Development of high-strength magnesium alloys for degradable implant applications

Introduction and design principles

In osteosynthesis, high-strength Mg alloys are especially attractive because of their mechanical characteristics and in particular because of the closeness of their Young’s modulus to that of human bone [21]. Because Mg implants do not have to be removed after the bone has healed, the burdens on both the patient and the health care system are reduced. Demand for suitable Mg alloys for applications in osteosynthesis is therefore increasing. During the last few decades considerable efforts to develop high-strength Mg alloys were made, but mostly in the field of automotive applications, e.g. [22, 23]. These Mg alloys feature attractive strength values at generally low ductility, and are mostly unsuitable for implant applications because of their insufficient electrochemical and/or biological performance. In the following, the requirements and the design strategy employed for the development of high-strength Mg alloys for degradable implant applications in osteosynthesis are presented.

When evaluating the potential of Mg alloys for applications in osteosynthesis the mechanical, electrochemical and biological properties have to be considered. From a mechanical point of view, osteosynthesis applications require in particular a combination of high strength and reasonable ductility, to provide adequate support to the fractured bone and to allow a sufficient plastic deformation tolerance on the part of the device during implantation (e.g. when plates must be bent to fit the bone, or in screw fixation). From an electrochemical point of view, fairly slow and homogeneous degradation of the alloy is desirable to assist the tissue healing process and to prevent the formation of hydrogen gas pockets upon Mg degradation. Biologically, the material and substances released during degradation must not be harmful to the human body.

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2 See also P. Gunde, A.C. Häni, A.S. Sologubenko, P.J. Uggowitzer, Materials Science and Engineering A (accepted).
Grain refinement of Mg alloys is a well known efficient approach for enhancing both the strength and the ductility of the material [18]. Upon grain refinement the strength of an alloy is enhanced by grain boundary hardening described by the Hall-Petch relationship [24, 25], and the ductility is increased due to activation of non-basal slip deformation modes based on compatibility stresses near grain boundaries [26, 27]. Recently, design strategies aiming at substantial grain refinement via industrial processing routes (also the objective of this study) have been developed [12, 13]. They consider the grain-growth-inhibiting potential of solutes during solidification [18], represented by the growth restriction factor (GRF), and the dragging influence of second phase particles on the grain boundaries during extrusion, represented by the Zener pinning pressure [28, 29]. Further increase in strength may subsequently be gained by precipitation hardening, which in turn can be triggered by specific ageing heat treatments after extrusion.

The Mg–Zn–Zr(–RE) alloying system is very attractive for designing material properties because it allows the formation of grain-refined, and thus high-strength, reasonably ductile and also age-hardenable Mg alloys, e.g. [12, 30], that in addition are particularly tolerant of slight deviations in composition while maintaining the overall performance. Therefore, this system was used as a basis for this work. With respect to electrochemical and biological properties, however, further alloying elements were carefully selected because many alloying additions may either have a detrimental effect on the degradation performance due to the formation of microgalvanic elements and electrochemical potential differences, or they may be harmful to the body. In addition to Zn and Zr, in this work Ca, Mn and Yb were chosen as further alloying elements. The alloy compositions are indicated in Table 3.2.1 and the reasons for the selection of the alloying elements are explained below.

In a previous study the Mg–Zn–Ag–Ca–Mn(–Zr) alloying system was developed and the performance of as-extruded Mg-3Zn-0.5Ag-0.25Ca-0.15Mn(-0.5Zr) (in wt.%) alloys was investigated, particularly with respect to microstructural and mechanical properties [12, 13, 31]. The Zr-free alloy was found to exhibit very high tensile elongation (27%) at reasonable strength (ultimate tensile strength (UTS) of 250 MPa),
while the alloy with Zr exhibited high strength (UTS of 350 MPa) at a considerable tensile elongation (21%). Therefore, owing to the promising combination of high strength and remarkable ductility, this Zr-containing alloy (despite its not-yet-optimal electrochemical performance), provided a basis for the alloys presented in this study and serves as reference material. To enhance the performance of this Mg-3Zn-0.5Ag-0.25Ca-0.15Mn-0.5Zr alloy, particularly in the context of its potential application in osteosynthesis, the composition was adapted (see Table 3.2.1) and the influence of the rare earth element Yb on the alloy’s property profile was studied.

Zirconium yielded a significant reduction in grain size (see [12]). In comparison with earlier studies [12, 13, 31], in this work the amount of Zn was increased to 5 wt.% for three reasons: (i) to improve castability; (ii) to increase the GRF during solidification (see below); and (iii) to enhance the alloy’s age hardening response [30]. The amount of Ca and Mn were kept at rather low levels. Calcium was added mainly for its grain refining effect both during solidification (considerable GRF, [12, 18]) and during extrusion (formation of fine grain-boundary-pinning Ca–Mg–Zn intermetallics as found in the alloys in [12] and also in Mg–Zn–Zr–RE–Ca alloys [32]. Additionally, the combined addition of Zr and Ca was reported to enhance the refinement of castings [33]. Manganese was added to convert heavy metal impurities, which are detrimental to corrosion resistance, into compounds that sediment during alloy melting [34]. The reasons for the Yb addition were the following. Ytterbium is soluble in Mg [35] and yields considerable growth restriction during solidification [18]. It was also observed that the solidus temperature ($T_s$) of the castings was raised upon the addition of Yb. This increase in $T_s$ results in a smaller terminal freezing range (TFR) than that of the Yb-free alloy and, because the TFR correlates with the hot tearing susceptibility (see chapter 3.1), it also causes a reduction in the (generally high) hot tearing susceptibility of Mg–Zn alloys. Figure 3.2.1 shows Scheil calculations of the TFR of the Yb-free alloy, which were performed using the Pandat software (PanMg8 database) [16]. The solidus temperature derived from differential scanning calorimetry measurements (DSC) of the Yb-containing alloy was included manually because the element Yb is not (yet) available in the database. Other reasons for choosing Yb were
its beneficial influence on the corrosion resistance of Mg–Zn alloys [36] and on the age hardening potential of Mg–Yb alloys [35]. Although a higher RE content was shown to increase the strength and hardness of Mg–Zn–Zr–RE alloys [22], Yb addition was not exaggerated because of its potential influence on inflammatory genes in human cells [37]. To study the influence of Yb on the properties of the Mg–Zn–Zr–Ca–Mn system, both Yb-free and Yb-containing alloys were produced.

![Thermodynamic calculations](image)

**Figure 3.2.1:** Thermodynamic calculations after Scheil for the terminal freezing range of the alloy ZKCa50, and (manually included) the solidus temperature of ZYbK520, measured by DSC.

**Experimental**

**Sample preparation**

The alloys with the compositions given in Table 3.2.1, denoted as ZKCa50 (Yb-free alloy) and ZYbK520 (Yb-containing alloy), were cast by vertical direct chill casting on an industrial scale (billet diameter: 185 mm). Magnesium and the alloying elements were first melted in an electric furnace at a temperature of approximately 690°C and then cast at a speed of approximately 1.6 mm s\(^{-1}\) with continuous water-cooling. Afterwards, the castings were formed by direct extrusion: the extrusion ratio was approximately 30:1, the speed 0.3–0.6 mm s\(^{-1}\) and the temperature of the recipient 300°C for both alloys. To avoid dissolution of the grain-boundary-pinning particles, which formed during solidification (Zn–Zr or Ca–Mg–Zn intermetallic phases (IMP)),
the extrusion temperature was chosen carefully based on thermodynamic calculations using the Pandat software and DSC analysis.

<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>Mg</th>
<th>Zn</th>
<th>Zr</th>
<th>Ca</th>
<th>Mn</th>
<th>Yb</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZKCa50</td>
<td>balance</td>
<td>5</td>
<td>0.3</td>
<td>0.25</td>
<td>0.1</td>
<td>–</td>
</tr>
<tr>
<td>ZYbK520</td>
<td>balance</td>
<td>5</td>
<td>0.3</td>
<td>0.25</td>
<td>0.1</td>
<td>2</td>
</tr>
</tbody>
</table>

In order to modify mechanical properties of the alloys, heat treatments at different temperatures and for various time periods were performed and their influence on microstructural and mechanical properties were studied. The temperatures and durations were chosen so as to avoid grain growth. To induce recrystallisation, a recrystallisation heat treatment (RHT) at 360°C (well below the T_s of the extrusions) for various time periods in the range of 0.5–168 h was carried out for both alloys. Afterwards, the 4h/RHT and 48h/RHT samples, differing by their degree of recrystallisation, were subjected to a brief solution heat treatment (SHT) at 379°C and 387°C for ZKCa50 and ZYbK520, respectively, which is approximately 15 K below the corresponding T_s. Due to the relatively high SHT temperatures, the SHT was performed for only 0.25, 0.5 and 1 h to avoid grain growth. Both RHT and SHT were carried out in an air-circulating oven. Additionally, an ageing heat treatment was performed on 4h/RHT and 48h/RHT samples, and on RHT+0.5h/SHT samples. The ageing was performed at 160°C in an oil bath for various periods of time (up to 72 h) and assessed by the Vickers hardness measurements carried out on a regular basis. Altogether, four heat treatment states of Yb-free and Yb-containing alloys were studied: as-extruded, RHT, RHT+SHT, and RHT+SHT+ageing.

The mechanical properties of the as-extruded and the variously heat-treated material were evaluated by standard tensile and compression tests at room temperature. The cylindrical tensile specimens had a gauge length of 18 mm and a diameter of 3 mm, and the compression samples measured 5 mm in diameter and 10 mm in length. The crosshead speeds were 1.08 mm min⁻¹ and 0.6 mm min⁻¹ for the tension and compression tests, respectively, corresponding to an initial strain rate of 10⁻³ s⁻¹. Three samples were tested per condition.
Characterisation of the microstructure

Microstructure analysis of the castings and the heat-treated material was performed by optical microscopy (OM), scanning electron (SEM) and transmission electron microscopy (TEM). The samples for OM and SEM studies were first ground, polished and then etched with acetic-picric acid (1 g picric acid, 5 ml acetic acid, 10 ml deionised water, 100 ml ethanol). The average grain size was determined using the linear intercept method. SEM analysis was performed on a Hitachi SU-70 microscope operated at 10 kV in the secondary electron (SE) and back-scattered electron (BSE) imaging modes. Conventional TEM (CTEM) and scanning transmission electron microscopy (STEM) studies, complemented by energy dispersive X-ray (EDX) analysis in the STEM mode, were employed for the morphological and phase analysis of the alloys of interest. STEM was performed in a high-angle annular dark-field (HAADF) operation mode using a 0.6–0.8 nm probe size. TEM studies were performed on a FEI Tecnai F30 machine (operated at 300 kV). For TEM, thin disks of 3 mm in diameter were first mechanically ground to a thickness of about 100 μm, and further thinned down to approximately 20–30 μm by dimple grinding on both sides on a Gatan dimple grinder. Electron transparency was achieved by chemical etching of the dimpled foils for a few tens of seconds in a solution of 90 vol.% methanol and 10 vol.% nitric acid performed at room temperature. The chemical etching of the foils was carried out immediately before the TEM sessions, to minimise the imaging artefacts due to the oxidation and contamination of the foils.

Results

Metallographic characterisation

The cross-sections of the castings of both alloys featured a homogeneous and very fine-grained microstructure across the billet diameter, as shown in Fig. 3.2.2a and b. The grain-refining effect of Yb is clearly visible. Upon its addition the grain size decreased from 100±15 μm in ZKCa50 (Fig. 3.2.2a) to 70±10 μm in ZYbK520 (Fig. 3.2.2b). In both alloys the shape of the grains was globular, and intermetallic (eutectic)
phases were found at the grain boundaries. After extrusion, both alloys exhibited a fine-grained microstructure with grains of less than 2 µm in size (Fig. 3.2.2c, d). The grain size of the Yb-containing alloy (Fig. 3.2.2d) was slightly smaller than that of the Yb-free alloy (Fig. 3.2.2c) at the same extrusion conditions. However, in the centre of

![Micrographs](image_url)

Figure 3.2.2: Optical micrographs of (a, b) the as-cast and (c, d) the as-extruded material of (a, c) the Yb-free ZKCa50 and (b, d) the Yb-containing ZYbK520 alloys. Due to etching artefacts the precipitates appear larger than they really are.

all extruded bars, “worm-like” sections of the microstructure were observed by optical microscopy (Fig. 3.2.3a) evidencing the incomplete dynamic recrystallisation, which is typical in many Zr-containing Mg alloys [38]. After annealing at 360°C (48h/RHT) recrystallisation was observed, accompanied by the disappearance of the “worm-like” sections (Fig. 3.2.3b, c) and slight growth of the grain size and IMP particles (Fig. 3.2.3c). Generally, in both alloys the grain size remained small (average grain size reached ~2.5 µm for 48h/RHT, with individual grains growing up to approximately 5–10 µm). Simultaneously, the hardness of ZYbK520 alloys continuously decreased from
80–85 HV in the as-extruded state to approximately 70 HV after 48h/RHT. The hardness values of the Yb-free alloy were generally slightly lower. The subsequent SHT of the recrystallised material led to an additional marginal reduction in hardness and to slight grain growth for both alloys; the average grain size reached ~4 µm after 48h/RHT+1h/SHT. The ageing heat treatment at 160°C produced an increase in hardness. In both alloys hardness peak values of 75–80 HV were reached after around 24 h of ageing, representing an increase of 10–15%. Upon further ageing the hardness decreased only slightly.

Figure 3.2.3: Optical images of the central area of the ZYbK520 alloy in (a) the as-extruded and (b, c) the 48h/RHT state. Due to etching artefacts the precipitates appear larger than they are in reality.

**Mechanical performance**

Tensile tests on the as-extruded material revealed high yield and tensile stress values at a high ductility for both alloys (Table 3.2.2). In general, the Yb-free alloy exhibited slightly lower yield stress at higher ductility compared to ZYbK520. For ZKCa50, yield and tensile stresses of 330 and 360 MPa were achieved at an elongation to fracture value of 19%. For ZYbK520, an even higher yield stress value of 350 MPa was obtained at an elongation to fracture of 15%. In both alloys the uniform elongation was around 10%. The RHT had a positive influence on the ductility of both alloys even if maximum recrystallisation could not be achieved (as indicated by the strain hardening behaviour of the Yb-containing alloy presented in Fig. 3.2.4): uniform elongations over 10% and elongations to fracture of more than 20% were reached. With increasing RHT time, the yield and tensile stress decreased and the ductility increased; after 48h/RHT, minimum yield stresses of 210 and 230 MPa at an
Table 3.2.2: Mechanical properties in compression and tension of the as-extruded and heat-treated alloys ZKCa50 and ZYbK520 at room temperature (standard deviation of stress data <10%; standard deviation of strain data <20%).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>state</th>
<th>$\sigma_{0.2,t}$</th>
<th>$\sigma_{UTS}$</th>
<th>$\varepsilon_a$</th>
<th>$\varepsilon_r^*$</th>
<th>$\sigma_{0.2,c}$</th>
<th>$\sigma_{0.2,t} / \sigma_{0.2,c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZKCa50</td>
<td>as-extruded</td>
<td>330</td>
<td>365</td>
<td>10.5</td>
<td>19.5</td>
<td>270</td>
<td>1.22</td>
</tr>
<tr>
<td>ZKCa50</td>
<td>4h/RHT</td>
<td>260</td>
<td>320</td>
<td>13.5</td>
<td>24</td>
<td>220</td>
<td>1.18</td>
</tr>
<tr>
<td>ZKCa50</td>
<td>4h/RHT+24h ageing</td>
<td>305</td>
<td>330</td>
<td>10</td>
<td>23</td>
<td>240</td>
<td>1.27</td>
</tr>
<tr>
<td>ZKCa50</td>
<td>4h/RHT+0.5h/SHT+24h ageing</td>
<td>305</td>
<td>345</td>
<td>10</td>
<td>19.5</td>
<td>240</td>
<td>1.27</td>
</tr>
<tr>
<td>ZKCa50</td>
<td>48h/RHT</td>
<td>210</td>
<td>295</td>
<td>18</td>
<td>26</td>
<td>190</td>
<td>1.11</td>
</tr>
<tr>
<td>ZKCa50</td>
<td>48h/RHT+24h ageing</td>
<td>250</td>
<td>305</td>
<td>12.5</td>
<td>25.5</td>
<td>210</td>
<td>1.19</td>
</tr>
<tr>
<td>ZKCa50</td>
<td>48h/RHT+0.5h/SHT+24h ageing</td>
<td>260</td>
<td>310</td>
<td>12</td>
<td>24</td>
<td>225</td>
<td>1.16</td>
</tr>
<tr>
<td>ZYbK520</td>
<td>as-extruded</td>
<td>350</td>
<td>360</td>
<td>8</td>
<td>16.5</td>
<td>280</td>
<td>1.25</td>
</tr>
<tr>
<td>ZYbK520</td>
<td>4h/RHT</td>
<td>285</td>
<td>325</td>
<td>12</td>
<td>23</td>
<td>230</td>
<td>1.24</td>
</tr>
<tr>
<td>ZYbK520</td>
<td>4h/RHT+24h ageing</td>
<td>305</td>
<td>330</td>
<td>10</td>
<td>24.5</td>
<td>240</td>
<td>1.27</td>
</tr>
<tr>
<td>ZYbK520</td>
<td>4h/RHT+0.5h/SHT+24h ageing</td>
<td>315</td>
<td>345</td>
<td>11</td>
<td>20.5</td>
<td>235</td>
<td>1.34</td>
</tr>
<tr>
<td>ZYbK520</td>
<td>48h/RHT</td>
<td>230</td>
<td>295</td>
<td>14.5</td>
<td>23.5</td>
<td>205</td>
<td>1.12</td>
</tr>
<tr>
<td>ZYbK520</td>
<td>48h/RHT+24h ageing</td>
<td>260</td>
<td>300</td>
<td>12.5</td>
<td>21.5</td>
<td>215</td>
<td>1.21</td>
</tr>
<tr>
<td>ZYbK520</td>
<td>48h/RHT+0.5h/SHT+24h ageing</td>
<td>275</td>
<td>315</td>
<td>12</td>
<td>22</td>
<td>230</td>
<td>1.20</td>
</tr>
</tbody>
</table>

* $\sigma_{0.2,t}$: yield stress in tension, $\sigma_{UTS}$: ultimate tensile stress, $\varepsilon_r$: uniform elongation, $\varepsilon_r$: elongation to fracture, $\sigma_{0.2,c}$: yield stress in compression. RHT was performed at 360°C, SHT at 379°C for ZKCa50 and at 387°C for ZYbK520, and ageing at 160°C.

Figure 3.2.4: Stress-strain diagram of as-extruded ZKCa50 and ZYbK520, and ZYbK520 in various heat treatment states.

elongation to fracture of 26% and 23.5% for ZKCa50 and ZYbCa520, respectively, were measured. Upon the subsequent ageing at 160°C, the yield stress increased again by 15–20%, accompanied by only a marginal loss of ductility. The brief SHT prior to
the ageing resulted in a slight rise in yield and tensile stress values compared to the non-SHT state for both alloys.

In both alloys, the RHT also had a positive influence on the tension-compression yield stress asymmetry, which was generally low. In compression, the yield stress was lower than in tension for all heat treatment states. In all the as-extruded material the tension-compression yield stress asymmetry was approximately 1.25 and generally decreased with RHT time, subsequently slightly increasing again due to ageing.

**SEM and TEM studies**

SEM and TEM analysis was performed on both alloys. As the microstructural features were similar and as the focus lay on the influence of Yb on the alloy properties, only the results of the Yb-containing alloy ZYbK520 are presented. The TEM morphological analysis of the as-extruded ZYbK520 alloy (Fig. 3.2.5) revealed a not completely recrystallised grain morphology and a high density of lattice defects. The OM observations of the as-extruded and 48h/RHT ZYbK520 alloy (Fig. 3.2.3a-c) complement these TEM results showing that hot extrusion and the subsequent heat treatments did not result in complete dynamic and static recrystallisation. In addition,

![Figure 3.2.5: BF TEM image of a polycrystalline region in as-extruded ZYbK520. The grain morphology and the high dislocation density within the grains evidence the incomplete recrystallisation. The black areas, labelled “I”, correspond to the (Yb, Ca)–Mg–Zn IMP particles.](image)
the SEM micrographs (Fig. 3.2.6a, b), taken in the back-scattered electron (BSE) imaging mode and thus featuring the chemical contrast, show the presence of heavy-atom-enriched IMP particles decorating grain boundaries and lattice defects (small bright spots in the images marked with black arrows for the grain boundary and with white arrows for the lattice defect decorations). The comparison of the images in Fig. 3.2.6 demonstrates that the IMP particles grow upon heat treatment.

![SEM micrographs](image)

Figure 3.2.6: BSE SEM images of the ZYbK520 alloy acquired from specimens in (a) the as-extruded and (b) the 48h/RHT state. Very dark areas in the image are artefacts due to preferential etching. Black arrows point to grain boundaries decorated with second phase particles. White arrows mark dislocations or small-angle grain boundaries pinned by IMP particles.

Microstructural analysis of the Yb-containing alloys in all heat treatment states by CTEM, SEM and HAADF-STEM (the latter two are atomic number sensitive) revealed that a few distinctly different types of IMP particles occur in the material. Upon heat treatments, all IMP particles grow and evolve (compare Fig. 3.2.6a with 3.2.6b and the vertical rows of images in Fig. 3.2.7). The comparison of the particle morphologies allows to suggest the occurrence of three different intermetallic phases in the Yb-containing alloys.

(i) Large globular particles of about 0.5–2 μm in size are the most prominent and of the largest volume fraction. They were found predominantly at the matrix grain boundaries and were observed by OM, SEM and TEM. They are seen as large black areas in the TEM micrograph in Fig. 3.2.5 and they are the largest and brightest particles in the SEM image in Fig. 3.2.6a.
Figure 3.2.7: HAADF-STEM micrographs of ZYbK520 in (a, d) the as-extruded, (b, e) the 48h/RHT, and (c, f) the 48h/RHT+0.5h/SHT+peak-aged state. The (a, b, c) images are taken at lower and the (d, e, f) images at higher magnifications. The latter were acquired from singular grains in high symmetry zone axis orientations (the large white arrows indicate the c direction of the matrix crystal). They show the intra-granular defect structure and specific crystallographic correspondence of the matrix and the IMP particles. Black arrows mark grain boundaries decorated with IMP particles. The small white arrows indicate dislocations or small-angle grain boundaries pinned by IMP particles. The (g, h, i) images are schematics illustrating the crystallographic correspondence of the rod- and plate-like IMP particles and the matrix in (g) the as-extruded, (h) the 48h/RHT, and (i) the 48h/RHT+0.5h/SHT+peak-aged state. The rod-like particles are parallel to the c direction of the α-Mg whereas the plate-like particles lie on the matrix basal planes. The increase in number density and size of the IMP particles upon heat treatments can be seen from the image comparison.

(ii) Roughly spherical, a few nanometer large particles (depending on the heat treatment state the diameter ranges from 3–50 nm) were observed at the (small-angle) grain boundaries and dislocations (short white arrows in Fig. 3.2.6 and Fig. 3.2.7). Larger particles tend to be located at grain boundaries, as seen in Fig. 3.2.7a-c. In the
as-extruded state (Fig. 3.2.6a, Fig. 3.2.7a), the diameter of these IMP particles ranged from 10–15 nm for particles pinning the grain boundaries and from 3–10 nm for those decorating the small-angle grain boundaries and dislocations. Upon 48h/RHT, these particles grew to approximately 15–50 nm (see Fig. 3.2.7b). No significant particle growth was observed upon the subsequent SHT+ageing heat treatments (see Fig. 3.2.7b, c).

(iii) The third type of second phase particles are rod- and plate-like IMP particles found at dislocations and in defect-free regions of the matrix grain (Fig. 3.2.7d-f). The rods are aligned perpendicular to the basal planes of \( \alpha \)-Mg (elongated in the \( c \) direction of the \( \alpha \)-Mg lattice), whereas the plates are parallel to the basal planes of \( \alpha \)-Mg. Among all second phases, these rod- and plate-like particles grew the most upon each heat treatment step (Fig. 3.2.7d-f). Additionally, ageing induced a significant increase in the volume fraction of these rods and plates (compare Fig. 3.2.7e and 3.2.7f and see schematic in Fig. 3.2.7g-i).

![Figure 3.2.8: BF TEM micrograph acquired in the [01 \( \bar{1} \)0] zone axis orientation of a 48h/RHT ZYbK520 grain. The interactions of roughly spherical IMP particles with small-angle grain boundaries can be seen (arrowed). The rod- and plate-like particles are also present, but hardly visible in the image.](image)

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The TEM micrograph of a 48h/RHT ZYbK520 specimen (Fig. 3.2.8) shows the interactions of roughly spherical IMP particles (arrowed) with lattice defects. These IMP particles pin the dislocations and most predominantly the small-angle grain boundaries (arrows in Fig. 3.2.8 point to some particles on small-angle grain boundaries). In this image, the rod- and plate-shaped precipitates are barely visible due to their small size and thus low contrast, but in higher magnification CTEM images the rods and plates were discerned.

EDX analysis indicated the presence of Mg and Zn in the α-matrix. In the case of the largest, micrometer-sized IMP particles, Mg, Zn, Yb and Ca signals were detected. According to EDX-data, the roughly spherical IMP particles contain the elements Mg, Zn, Zr and Mn, while only Mg and Zn were found in the rod- and plate-like particles.

**Discussion**

**Design principles**

As a result of our design strategy, efficient grain refinement during solidification was achieved in both the Yb-free and Yb-containing alloys. Considering that identical casting parameters were used, the slightly smaller grain size in ZYbK520 is ascribed to the supplemental grain-growth-restricting influence of ytterbium. The somewhat larger grain size of our castings compared to similar Mg–Zn–Zr–Ca alloys in [12, 30] is accredited mainly to the differences in casting conditions, in particular the lower cooling rates. After the thermo-mechanical processing, the grain size of the ZKCa50 and ZYbK520 alloys was very small and similar to that reported in [12, 30]. We attribute this fact to the fine microstructures of the castings, the appropriately chosen extrusion parameters and the presence of grain-boundary-pinning IMP particles, which hinder grain growth during thermo-mechanical forming. Our analyses show that the degree of recrystallisation was moderate in as-extruded alloys, but noticeably enhanced in RHT specimens. Complete recrystallisation, however, could not be achieved in our experiments. We explain this by the effect of IMP particles on the lattice defects’ mobility.
Microstructural and mechanical performance

Evaluation of the mechanical properties by tensile and compressive testing shows a good combination of strength and ductility for both alloys in all states (as-extruded and heat-treated). Moreover, the tests reveal that the appropriate choice of heat treatment parameters enables control over the alloys’ stress-strain performance. The attractive mechanical properties of the alloys can principally be attributed to the appropriately designed fine-grained alloy microstructures that result in reduced grain boundary mobility, which strengthens the alloy (as described by Hall-Petch). Moreover, a fine-grained microstructure promotes the activation of complementary deformation processes (the deformation mechanisms and their dependence on the composition and microstructural states of the alloys are not included in this work) enhancing ductility of the alloys, as seen also in [26, 27]. In addition, the presence and formation of second phase particles of different morphologies on the lattice defects leads to effective pinning of the dislocations and the abundant small-angle grain boundaries. As a consequence the dislocation mobility is lowered and the strength is enhanced.

The high yield strength in the as-extruded state is mainly attributed to the fine-grained microstructure and the impediment of dislocation motion due to the high defect density. Upon RHT slight grain growth and recrystallisation occur, facilitating dislocation movement and causing a decrease in tensile and compressive yield stress. Age hardening, on the other hand, results in an increase in volume fraction and size of the rod- and plate-like IMP particles in the matrix grain, contributing to the increase in yield stress. From the morphological and chemical analysis of these particles it is assumed that the small rod- and plate-like IMP particles that were also found in the Yb-free alloy represent the same Mg–Zn hardening phase (MgZn2) as reported by Mendis et al. [30]. However, for a confident identification of this phase further studies are necessary.

Besides their attractive combination of strength and ductility, another advantage of our alloys is their low tension-compression yield stress asymmetry, which is mainly ascribed to the small grain size [27]. It is known for Mg alloys that with decreasing
grain size an activation of the twinning deformation mode becomes increasingly difficult because of the large energy of twin interfaces. The energy caused by grain boundary incompatibility stresses is assumed to be consumed first by non-basal slip than twin formation [27]. Upon the RHT, the tension-compression yield stress asymmetry decreases in all alloys compared to the as-extruded state. The reason for this effect is assumed to be the decreased dislocation density and the associated reduced stress concentrations at which twinning would preferentially be initiated. Upon ageing, however, the tension-compression yield stress asymmetry increases slightly. We assume that this can be attributed to the prompt and extensive increase of the volume fraction of coherent rod-like IMP particles (detected by TEM, Fig.7f), which on the one hand decorate dislocations and impede their motion and on the other hand enhance twinning because of stress concentrations related to them. A similar effect is suggested to take place also in the material after the RHT+SHT+ageing treatment.

**Influence of ytterbium**

Ytterbium is not a widely employed alloying element for Mg alloys and has rarely been used in Mg technology. Therefore only little literature data exist about the effect of Yb on the mechanical behaviour of Mg alloys. Thus we present its role in more detail in the following.

Due to the similar mechanical performance of ZKCa50 and ZYbK520 and the experimentally confirmed presence of ytterbium in the micrometer-sized IMP particles only, it is assumed that the element Yb exerts no significant influence on the active deformation and strengthening processes. However, the following effects can be attributed to ytterbium: (i) Yb reduces the alloy’s grain size due to its contribution to the grain growth restriction factor [18]; (ii) Yb reduces the hot tearing susceptibility during casting by increasing the solidus temperature and consequently decreasing the terminal freezing range (see chapter 3.1); and (iii) Yb is present in the large 0.5–2 μm IMP particles on the grain boundaries and thus contributes to grain-boundary pinning. It is noteworthy that Yb additions do not considerably increase the cost of the alloy
(price of Yb: circa 120 € kg⁻¹). From the EDX measurements of the Yb-containing IMP particles (in TEM foils) that show the presence of Yb only in large, grain-boundary-pinning particles, from Pandat calculations of the phase configurations of ZKCa30 [12], which predict the occurrence of Ca–Mg–Zn IMP particles (Ca₂Mg₆Zn₃), and taking into account the complete miscibility of Ca and Yb, it is suggested that the ternary (Ca, Yb)₂Mg₆Zn₃ phase has formed as large globular particles in the alloy ZYbK520. However, the precision of the EDX elemental analysis in TEM is not sufficient to make reliable conclusions about the exact composition of these IMP particles. These globular particles are likely to have formed during solidification of the remaining melt (eutectic phase).

When considering Yb as alloying element in our design strategy, it was expected that the addition of Yb would result in an improvement in the degradation resistance by incorporating Yb into the Mg matrix and in an increase in strength by the formation of Mg–Yb strengthening phases. EDX measurements, however, indicate no Yb signals in the matrix or in the small IMP particles. It is likely that all Yb added to the melt becomes consumed by the (Ca, Yb)–Mg–Zn phases. This fact that no Yb was found solved in the α-Mg matrix implies two conclusions. In contrast to observations reported in [35] or [39], no Yb-containing strengthening phases form, and the corrosion behaviour is not particularly improved, as the matrix is not rendered nobler.

To increase the corrosion resistance, surface treatments similar to those in chapter 2 were investigated. However, they also did not bring about the desired improvement. The heat treatments were performed at rather low temperature (360°C) for various time periods, so as to not destroy the alloys’ attractive mechanical properties by grain growth or formation of a liquid phase. SEM and EDX analysis revealed an uneven oxidised surface layer, where the microstructure of the bulk underneath was still visible in the BSE SEM images, and with inhomogeneous composition. It seems that three distinctive oxides formed. In most parts of the surface (i.e. grain interior of the substrate), the elements Mg, Ca, O, Yb and some Zn were detected. In the areas close to the large IMPs, oxygen, Ca, Zn and Yb were measured in relatively high amounts. In a few spots only, Yb and O were enriched. Due to their inhomogeneity, the surface
oxidised samples were not further considered for implant materials. Then, a second sample series was coated with a 10 μm thick Magoxid-coat® deposited by AHC Oberflächentechnik GmbH, Germany. Immersion testing revealed initial protection of the substrate by the coating and thus reduced hydrogen gas production. However, relatively soon the coatings were penetrated (leading to inhomogeneous corrosion attack) and degradation of the substrate underneath occurred. In the third approach, samples were electroplated with Zn. It turned out, however, that due to the high reactivity of the alloys, the chemical Zn underlayer was not homogeneous and dense, resulting in defect-containing Zn electroplatings. To summarise, none of the surface treatments on ZKCa50 and ZYbK520 evaluated in this work led to significant improvement of the degradation performance. Among the tested coatings, the Magoxid-coat® seemed to be the most suitable.

**Summarising comments**

Figure 3.2.9 presents a review of the yield stress versus elongation to fracture performance of Mg–Zn based alloys potentially suitable for medical applications [12, 13, 30, 39-41]. The data also give a comparison to the performance of the newly developed alloys. All alloys presented in the figure were produced similarly to ours: they were cast and then hot extruded, with extrusion ratios between 10:1 and 30:1. It can be observed that our extruded alloys are situated in the upper central area of the diagram, i.e. they exhibit a high yield stress at moderate fracture strain. In the as-extruded state, they feature significantly higher yield stress at improved ductility in comparison to the commercial alloys ZK31 or ZK60. In addition, high-strength alloys presented in literature which show tensile yield stresses similar to our alloys predominantly feature a significantly lower fracture strain, e.g. [41]. The RHT (with and without subsequent ageing) results in a shift of our alloys’ mechanical performance towards an improvement of fracture strain and a decrease in yield stress. Only alloys ZQCa30, WZ21 and ZW21, which were developed for applications in vascular intervention (where a high uniform elongation at moderate strength is important), and the Mg-6Zn-0.4Ag-0.2Ca alloy, which is similar to ZQCa30, feature
higher ductility than our heat-treated material, however also at much lower strength. In summary, high-strength Mg alloys were developed where the strength-ductility relation can be tailored by appropriate heat treatments.

**Conclusions**

In this study Mg–Zn–Zr–Ca–Mn(–Yb) alloys were developed which exhibit high strength (yield stress up to 350 MPa) at considerable ductility (fracture strain >15%) and relatively low tension-compression yield stress asymmetries. The design approach presented in this work involved grain growth restriction mechanisms which act during solidification (solute drag) and thermo-mechanical processing (grain-boundary-pinning). The extraordinary combination of high yield strength and high ductility obtained upon thermo-mechanical processing and subsequent heat treatments is attributed to the fine-grained microstructure, and the optimally dispersed lattice-defect-pinning IMP particles, i.e. (small-angle) grain-boundary- and dislocation-pinning. The high ductility of the material is mainly ascribed to the small grain size responsible for the activation of additional deformation modes (non-basal slip).
Moreover, the mechanical properties can be tailored by appropriate thermal treatments at different temperatures and for various time periods. From high strength in the as-extruded state a good combination of strength and ductility can be achieved upon subsequent annealing. This change in mechanical properties is explained by a slight increase in grain size, a reduction in lattice defect density during the recrystallisation heat treatments, and precipitation hardening.

The influence of Yb on the alloy performance was studied. The main functions of the Yb addition turned out to be the reduction of the hot tearing susceptibility during direct chill casting by decreasing the terminal freezing range, and the refinement of the microstructure of the cast and extruded material. Adding Yb to ZKCa50 significantly improved the alloy’s castability and improved its mechanical performance. Yb is found in grain-boundary-pinning particles, which hinder grain growth during hot extrusion and during subsequent heat treatments. To summarise, the mechanical performance is considered to be suitable for temporary implant application in osteosynthesis.
3.3 References

Chapter 4

Conclusions and outlook

4.1 Surface treatments

Surface treatments are a simple and efficient tool to protect the electrochemically active Mg and its alloys from the environment and improve the corrosion resistance. In Mg technology there exist various surface modification techniques. Many of them, however, lead to the formation of permanent, non-degradable coatings, which are not suitable for absorbable implants. Thus, in this study, various methods to produce degradable coatings to enhance the initial corrosion resistance were evaluated using the Mg–Y–RE alloy WE43 as substrate material. Due to its rather high corrosion resistance and its suitable mechanical properties, WE43 is a promising candidate as a degradable implant material.

In a first approach, thermal treatments at fairly high temperature (circa 500°C) for various times were performed in air to homogenise the Y distribution in the bulk (samples polished after the treatment are denoted in the following as “polished samples”) and to form a protective surface oxide layer (denoted as “oxidised samples”). Analysis of the thermal oxides revealed the presence of MgO and crystalline Y$_2$O$_3$ with varying thickness depending on the treatment time. Immersion testing in simulated body fluid of polished and oxidised samples indicated that the specimens degraded in different ways. The polished samples showed a high initial corrosion rate, which slowed with time due to the deposition of corrosion products on
the sample’s surface. This behaviour can be approximated by a parabolic law. The oxidised samples’ corrosion behaviour was low at the beginning and increased with time due to penetration or removal of the initially protective surface oxide. It followed a sigmoidal law. The corrosion performance of the oxidised samples depended on the oxide thickness, and was explained by a depletion hypothesis. There it was assumed that in briefly oxidised samples an yttrium-depleted zone underneath the oxide layer was present. As yttrium dissolved in the Mg matrix improves the corrosion resistance, the Y-depleted zone leads to significant hydrogen evolution upon break-down of the surface layer. In long oxidised samples, on the other hand, the Y-depletion was lower leading to a reduced maximum corrosion rate. To compare, the maximum degradation rate of annealed and polished samples was similar to the latter one. In summary, heat treatments are a simple method to improve the initial corrosion performance of Mg–Y alloys. One drawback of such surface oxides, however, is their brittleness. Upon bending and/or straining of an oxidised implant the layers crack and the corrosion resistance, measured in different body-similar and standard solutions, is decreased compared to intact oxidised samples. Compared to polished samples the corrosion resistance is still improved. Moreover, corrosion proceeded macroscopically homogeneous. In contrast, microstructural analysis revealed local corrosion attacks to start at the cracks and to proceed by undermining the oxide layer, eventually leading to a falling out of oxide fragments.

In a second approach, plasma-electrolytic oxidation coatings (Magoxid-coat®), where a porous ceramic oxide layer is formed, were industrially deposited. The degradation performance of samples with coating thicknesses of 5, 10 and 20 μm was tested in SBF in the non-loaded and also in the static uniaxial loaded state. It turned out that the coating provides protection at the beginning and is penetrated with immersion time causing hydrogen to evolve, when the samples are not loaded. Under static uniaxial load, however, stress corrosion cracking can occur leading to early fracture of the coated samples. Micro-cracks in the coating, which were already present in the non-loaded state, can propagate through the ceramic coating and into the metal. Thereby, metal comes into contact with the electrolyte and degrades locally
resulting in a decreased rupture life. In contrast, un-coated samples lasted relatively long and degraded in a homogeneous way. However, it can be assumed that in the human body the strain on the implant will be lower and thus the coated samples will survive longer.

To avoid the reduction of the corrosion resistance of the coatings by rupture due to deformation, ductile metallic coatings would be advantageous. Thus, in a third approach, the biologically also unproblematic Zn was electroplated on WE43. As zinc is nobler than magnesium, the coating must be uniform and homogeneous to avoid the occurrence of early galvanic corrosion. Due to the high activity of Mg and its alloys, a Zn underlayer, deposited by a chemical pre-treatment, is required prior to electroplating. In this work, a suitable chemical pre-treatment was developed and Zn was successfully electroplated from an alkaline and acidic electrolyte. However, the electroplatings revealed some inhomogeneities in the layer, which were more pronounced in the “acidic deposited” Zn coatings. These can originate from Zn-free areas in the Zn underlayer as there corrosion of the Mg substrate and consequently hydrogen gas evolution can occur when placing the samples in the electrolyte. Immersion tests revealed that these inhomogeneities in the acidic electroplated Zn coatings are possible sites for local corrosion attacks to start, which were observed after only a few hours of immersion. By alkaline electroplating prior to the acidic, the initial corrosion rate was improved, but the time for local corrosion attacks to occur was only slightly increased to approximately 1 day. In an attempt to improve the adhesive strength of the coating and thus the corrosion resistance, heat treatments were performed. They led to delamination of the alkaline deposited coating due to the presence of pores, and to the formation of a diffusion zone in the acidic electroplated coatings. In summary, the quality of the Zn coating produced in this work still shows potential for improvement.
4.2 Alloy development

It is known that a fine grain size has a positive influence on a Mg alloy’s properties, i.e. the mechanical properties and the structural uniformity are improved. Moreover, fine-grained castings prior to thermomechanical processing lead to improved properties of the material after forming. Thus, one aim of the alloy development was the achievement of a fine grain size during the course of production by an industrial processing route (i.e. direct chill casting (DCC) followed by extrusion). Moreover, the alloys should degrade in a slow and homogeneous way, and they should be tolerated by the human body. The design strategy developed in this thesis is based on a model by StJohn and Easton et al. Grain refinement during solidification should be achieved by the choice of suitable alloying elements, which have a high growth restriction factor $Q$ (a measure of the segregating power of an element), and which are not harmful to the human body. Grain growth during the subsequent thermomechanical processing should be avoided by the presence of grain-boundary-pinning particles. Among other common alloying elements for Mg, such as Zn or Zr, the element ytterbium was chosen in our alloys for the following reasons. Ytterbium features a considerable $Q$ value, it is highly soluble in Mg, it reduces the hot tearing susceptibility, it forms Mg–Yb hardening phases and it has been reported to improve the corrosion resistance of rapidly solidified Mg–Zn alloys.

The design concept elaborated resulted in fine-grained Mg–Zn–Zr–Ca(–Yb) alloys with attractive mechanical properties, i.e. high strength at moderate ductility and low tension-compression yield stress asymmetry. As-extruded material showed high yield strength (yield stress of up to 350 MPa) at an elongation to fracture of >15%. By thermal treatments, i.e. recrystallisation, solution and ageing heat treatments, the mechanical properties can be tailored. The ductility was significantly improved (elongation to fracture of approximately 20–25%), while the strength slightly decreased (yield stress values of 210–315 MPa). To our best knowledge this combination of strength and ductility has so far not been achieved in Mg–Zn alloys. These interesting mechanical properties can be mainly assigned to the fine grain size
of the alloys leading to grain boundary strengthening and activation of complementary deformation modes resulting in enhanced ductility. In addition, by SEM and TEM analysis the following factors were suggested to also improve the strength: incomplete recrystallisation resulting in high defect densities and interaction of dislocations with intermetallic phase (IMP) particles and/or (small-angle) grain boundaries; and Mg–Zn hardening phases forming in the matrix during the ageing treatment (precipitation strengthening). The increase in ductility and decrease in strength by the recrystallisation heat treatment is attributed to slight grain growth and recrystallisation facilitating dislocation movement.

Despite these attractive mechanical properties, the new Mg alloys are not yet ideal for applications in osteosynthesis, as their corrosion resistance is still rather low. Ytterbium, which should render the matrix nobler, is found only in large IMPs leading to internal galvanic corrosion in the vicinity of the IMPs. Even by surface modifications (those tested in this study were heat treatment, plasma-electrolytic oxidation and electro-plating of Zn), the corrosion resistance could not be significantly improved.

Heat treatments led to the formation of inhomogeneous surface oxide layers. Magoxid-coatings reduced the initial degradation rate; at the beginning of immersion only little gaseous hydrogen was produced. But they were soon penetrated (often within the first week) and local corrosion attacks were initiated. Electrochemical plating of Zn on these alloys was difficult to perform. Due to the high reactivity of the base alloy it was not possible to produce a homogeneous and dense Zn underlayer prior to electroplating. As a result, the Zn layers contained inhomogeneities, which impaired the degradation performance. In summary, the surface treatments evaluated in this study did not bring about significant improvement of the corrosion resistance of the new alloys ZKCa50 and ZYbK520. As the combination of mechanical, electrochemical and biological properties of an alloy is important when choosing a degradable implant material, it is suggested to further modify these alloys for applications in osteosynthesis.
However, the great benefit of ytterbium (and yttrium) is the positive influence on the casting process. By the addition of Yb, the hot tearing susceptibility (HTS) was significantly reduced and no cracks were observed in the DCC billet. To explain this phenomenon, additional Mg–Zn–Zr (i.e. Mg-3Zn-0.3Zr) alloys with systematically varied Yb and Y content, were produced by permanent star-shaped mould casting (PSM) and DCC (Y-containing alloys only), and thermodynamic calculations were performed. The dependence of HTS on the casting process was explained by the CSC (crack susceptibility coefficient) model of Clyne and Davies and by thermodynamic calculations of equilibrium (Lever) and non-equilibrium (Scheil) solidification. Moreover, taking this CSC model as a basis, it was shown that the HTS is related to the terminal freezing range (TFR). As the elements Y and Yb increase the solidus temperature and thus shorten the terminal solidification path and at the same time reduce the TFR, the HTS is reduced by their addition. The formation of a ternary Mg$_3$YZn$_6$ phase (analysed in the castings and also calculated by a “virtual alloy enrichment” approach) and Mg–Zn–Yb phase in the Y- and Yb-containing alloys, respectively, can be held responsible for the increase in solidus temperature. These findings are interesting not only for the casting of Mg alloys for implant materials, but also when producing alloys for the automotive industry, as the addition of Yb significantly reduces the hot tearing susceptibility without drastically increasing the cost of the alloy.

4.3 Outlook

It has been shown in this thesis that it is a difficult task to develop Mg alloys, which combine mechanical, electrochemical and biological properties suitable for bone implant applications. The mechanical properties of the newly developed ZKCa50 and ZYbK520 alloys were shown to be advantageous compared to the reference alloy WE43. The biocompatibility of the new alloys was not tested, but can be assumed to be similar to that of WE43. The corrosion resistance of the new alloys, however, was rather low, which is a major drawback. Future work should concentrate on the
improvement of the electrochemical performance of the new alloys, either by surface modification or – probably more promising – by adapting the alloy composition. Deposition of surface coatings by specialised industrial companies is suggested, as they are more experienced. Thereby, one possibility would be vapour deposition of high purity metallic Mg, which exhibits a rather high corrosion resistance.

The more promising route for improvement of the electrochemical properties without losing the mechanical and biological properties is by modification of the alloy composition. Thereby, the following considerations were made. For the new alloys, it is proposed to keep the Mn (0.15 wt.%) for melt cleaning and the Zr (0.3–0.5 wt.%) due to its positive influence on grain refinement and strength. The Zn-content of the alloys should be reduced to 2–3 wt.%. This is assumed to be sufficient Zn for solid solution strengthening, and at the same time the number of large Zn-containing intermetallic phase particles, which are not beneficial for the degradation resistance, is reduced. The relatively high hot tearing susceptibility of Mg–Zn alloys should be reduced, either by the addition of a small amount of Yb, or by choosing Y as additional alloying element, as yttrium is also known to be beneficial for the corrosion resistance. Due to the presence of Zr, the element Ca, which has a very high growth restriction factor, is not required and may or may not be added. Moreover, it can be thought about the addition of scandium. During this thesis Sc-containing Mg–Zn alloys, which were produced on a laboratory scale, were observed to have a positive influence on the corrosion resistance of the alloys. Thus, the Mg-(2–3)Zn-2Y-0.3Zr-0.15Mn is seen as a promising alloy composition for medical applications. Moreover, the Y could be replaced, e.g. by adding Yb (in low amounts to reduce the hot tearing susceptibility) and Sc (to improve the electrochemical properties).