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Klaus D. Jandt
Thomas F. Keller

The Effects of HAc Etching on the Degradation Behavior of Mg-5Gd

[1]*Marcjanna Maria Gawlik, [1]Markus Steiner, [1]Björn Wiese, [1]Jorge González, [1]Frank Feyerabend, [2]Michael Dahms, [1]Thomas Ebel, [1]Regine Willumeit-Römer

[1] Institute of Materials Research, Division Metallic Biomaterials, Helmholtz-Zentrum Geesthacht, Germany
[2]Hochschule Flensburg, Germany
*Corresponding author (marcjanna.gawlik@hzg.de)

Abstract – The effects of different acetic acid (HAc) etching procedures were investigated using Mg-5Gd samples in as-extruded and T4 conditions in order to achieve defined surfaces and homogenous degradation behavior. Samples were dipped into HAc solution with five different concentrations for three durations. In total, fifteen different etching conditions were tested with regard to the degradation resistance in physiological solution. The cell culture medium consisted of Dulbecco's Modified Eagle Medium (DMEM), Glutamax, 10 Vol.-% fetal bovine serum (FBS) and 1 Vol.-% Streptomycin/Penicillin solution. A screening test was performed to select the etching combinations with the lowest initial mean degradation depth. The most promising etching procedures were chosen for further long term degradation tests lasting up to 30 days in cell culture medium. The surfaces of the etched samples and for selected samples after degradation were characterized by interferometry, OM, SEM, and XRD to correlate the influence of morphology, roughness and microstructure on the degradation rate. Etching with 250 g/L HAc and 150 s leads to the most uniform degradation with low degradation rate compared to non-etched Mg-5Gd.

Keywords – acetic acid etching, biodegradable magnesium, degradation rate, surface characterization

1. INTRODUCTION

Mg degrades in aqueous solutions and produces a layer of magnesium hydroxide and hydrogen gas [1]. Aqueous salt solutions, including for example chloride ions, are particularly able to dissolve the protective magnesium hydroxide layer which leads to an acceleration of the degradation process [2]. Furthermore, impurities like Fe, Ni, Co and Cu or phases with high electrochemical potential difference to the Mg-matrix increase the degradation rate due to micro or macro galvanic corrosion [3]. To adjust the mechanical and degradation properties alloying elements and different processing steps are introduced. Mg alloys containing specific rare earth (RE) elements including Gd are used because their solubility increases with temperature which allows mechanical and degradation properties to be tailored by heat treatments. With a high solid solubility secondary phases are avoided, which improves the degradation behavior [4]. However, some Mg-RE alloys also contain hydride particles which can react with the Mg as galvanic cell and produce $Mg(OH)_2$ phases around these particles. Higher RE content in the alloy increases the amount of hydrides produced [5]. But it has been also reported that a content of Gd < 15.-wt % reduces the degradation rate [4]. Furthermore Gd was reported as an appropriate element in terms of cytoxicity for biodegradable materials [6]. Some reports confirm that the degradation behavior of Mg alloys can be improved by chemical surface treatments. Etching for example is an effective method for removing surface contaminations resulting from the production process [7, 8]. In addition, it removes twins near the surface region. Twins

act as additional weak points on the surface due to the reduction of the equilibrium potential at these locations [9]. Moreover, chemical surface treatments are able to improve the initial condition of the entire surface. This is necessary to achieve reproducible results regarding homogeneous degradation and linear degradation rate.

Aims of the study:

• Analyse the effects of acetic acid (HAc) etching on the morphology and microstructure of Mg-5Gd

• Evaluate the ideal surface treatment regardless of the processing route

• Ensure a reproducible degradation rate

2. MATERIAL AND METHODS

Material

For this study Mg-5Gd was used. Direct chill casting was performed with high purity Mg (99.95 %, Supplier: Magnesium Elektron) and Gd (>99.9 %) at 650 °C in a preheated mold. Afterwards the material was solution heat treated at 550 °C for 6 hours. The material was extruded at a speed of 3-4 mm/s at 430 °C. The diameter after extrusion was 12.0 mm. After machining, the rods were milled into discs with a diameter of 10.0 mm and a height of 1.5 mm. In the following, these discs are referred to as as-received samples (AR).

Etching procedure

The as-received samples were immersed in 3 ml hexane for 40 min in an ultrasonic bath to degrease the samples and to remove contaminations originating from production. HAc

solutions with concentrations of 100 g/L, 150 g/L, 200 g/L, 250 g/L and 300 g/L were prepared. The samples were immersed into a clock glass filled with 5 ml of HAc solution and samples were immersed for durations of 90 s, 120 s or 150 s. To stop the reaction, the samples were immersed in 40 mL of 1 mol/L NaOH for 30 s, followed by dipping these into 40 mL distilled water. After another dip into 40 mL of acetone and drying the sample with a piece of lint-free tissue, the samples were cleaned again in hexane for 40 min in an ultrasonic bath. After that, each sample was put into a falcon tube and filled with 3 ml of 70 % ethanol. The sterilization with ethanol necessary for the immersion tests under cell culture conditions was performed for 20 min in an ultrasonic bath. All specimens were weighed before and after cleaning and etching using an electronic balance (Sartorius, accuracy: 0.1 mg). To calculate the etching depth, the diameter and height of the discs were also measured before and after etching using callipers.

Degradation

• Short-term degradation test: To compare the effects of etching on the degradation behavior, 15 different testing series were analyzed by using a 24 h short term degradation test (n=6). The degradation behavior of the different samples was analyzed by immersing the samples into Dulbecco's Modified Eagle Medium (DMEN), Glutamax, 10 Vol.-% fetal bovine serum (FBS) and 1 Vol.-% of Streptomycin and Penicillin under cell culture conditions (37 °C, 5 % CO_2, 20 % O_2, 95 % relative humidity). After one day, six samples of each test series were taken out, washed with distilled water and dried for 24 h in a vacuum chamber. Following drying, the samples were weighed again. The degraded samples were treated with chromic acid for 20 min to remove the degradation layer. Afterwards, the specimens were dried for one hour and weighed again to calculate the weight of the corrosion layer. The mean degradation depth which can be considered the amount of surface removed was evaluated from mass loss using the formula:

$$d = \frac{\Delta m}{\rho \cdot A} \cdot 10^4 \qquad (1)$$

Here, d is the degradation depth in µm; Δm is the mass loss in g, measured by the weight before degradation and after removal of degradation products; ρ is the density in $\frac{g}{cm^3}$; A is the surface area in cm².

• Long-term degradation test: After evaluating the short-term degradation results, the etching methods with lowest mean degradation depths and standard deviations were used for the 30-day degradation tests. The preparation, degradation and removal processes were identical to those of the short-term test. In order to verify if etching with HAc affects the degradation behavior, as-received samples were also used for the degradation experiments. As-received samples received a minor additional treatment. They were put into falcon tubes filled with ethanol and then moved to the clean bench for further preparation. This procedure was executed to preserve the sterile area of the clean bench, where the degradation experiments were arranged. In the 30-day degradation test, one sample per day was removed out of the medium within the first week. Further samples were removed after every second day starting from the second week. In total 15 samples were measured per test series. The degradation depth was plotted over time. A linear fit was calculated over 15 measurement points. The slope of the linear fit is the degradation rate D. The degradation rate D was fitted linearly according to this formula as introduced by [10]:

$$d(t) = D \cdot t + do \qquad (2)$$

Here, d(t) is the degradation depth at time point t in µm; D is the degradation rate in µm/day; t is the time in days; d_o is the intersection of the linear fit with the y-axis.

Microstructure and surface characterization

• Microstructure: Metallographic preparation of cross sections was performed to analyze the deformation and twinning zone by optical microscopy (Leica DMI 5000 M). The twinning depth was measured by length measurement from the surface edge inwards into the sample by use of the Software analySIS pro. A mean value and standard deviation was calculated for as-received conditions using 18 positions.

• Interferometry: The surfaces of the samples were investigated at 5x magnification by an Interferometer (Bruker Contour GT-K) after etching and after the 30-day degradation period for one as-received sample and the evaluated combination of conditions. The surface topography and roughness was analyzed by the software Vision64. For surface characterization, the raw data was fitted using the F-Operator (cylinder and tilt) to remove the nominal shape. Afterwards the measured area was cut by use of the 3D Filter Mask Data into a measurement area of 8 mm to avoid effects from the surface edge region on the roughness. This was necessary due to the fact that some edges of the samples were damaged by the milling process.

• X-ray diffraction: Glancing angle x-ray diffraction was performed by Bruker D8 ADVANCED at an angle of 3°. Parallel beam setup was used with an aperture size of 0.6 µm. The measurements were carried out by a Cu anode (0.15418 nm). 2θ was set between 3° and 80°. Diffraction patterns were interpreted by the software DIFFRAC.EVA and Pearsons Crystal Data [11].

• SEM and EDX: The morphology was determined by Tescan Vega III SB after 2 days of degradation and removal of the degradation layer of the chosen combination of etching conditions. The analysis was carried out using 15 kV. The EDX point analysis and quantification was performed with the software Iridium Ultra.

3. RESULTS AND DISCUSSION

After 24 hours of short-term degradation it is visible in Figure 1 that the HAc etching reduces the mean degradation depth of Mg-5Gd in most cases. Only a combination of 100 g/L and 150 s does not decrease the mean degradation depth. The value of the mean degradation of the as-received Mg-5Gd samples is 3.1 ± 1.5 µm. The standard deviation of the as-received samples is higher compared to the etched conditions. Particularly, etching with a concentration of 150 g/L for 150 s leads to a reduction of the mean degradation depth. The combinations of 150 g/L for 150 s, 250 g/L for 150s and 300 g/L for 90 s were chosen for further long-term degradation testing due to their lowest mean degradation depth and standard deviation. Further results and

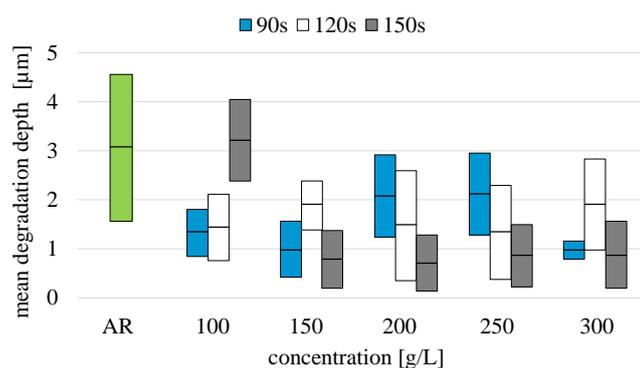discussions were carried out on the samples of these chosen conditions.

FIGURE 1
DIAGRAM OF THE MEAN DEGRADATION DEPTHS (ACCURACY: 0.3 μm) AND STANDARD DEVIATIONS OF 6 SAMPLES FOR EACH CONDITION AFTER 24 H SHORT-TERM DEGRADATION.

As-received samples show a difference in microstructure in regions near the surface and bulk material. Figure 2 illustrates the near-surface regions of one as-received sample and the etched samples. For the as-received sample, the grain structure is deformed, followed by high accumulation of twins. After etching it is visible that, for all etching conditions, the deformation zone is removed. Stronger twinning is only detectable for etching conditions of 150 g/L for 150 s and 300 g/L for 90 s. Comparison of the microstructures and the calculated etching depths reveals that the condition of 250 g/L for 150 s has the highest etching depth. It is the only condition that completely removes the microstructural changes originating from the production process whereas the conditions of 150 g/L for 150 s and 300 g/L for 90 s remove a similar amount of material corresponding to a comparable amount of remaining twins.
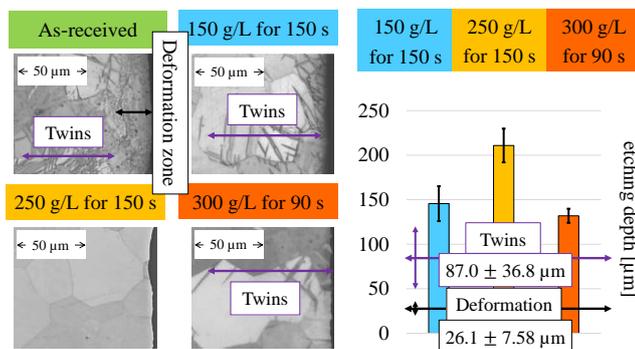

FIGURE 2
MICROSTRUCTURE OF THE CROSS SECTION OF ONE AS-RECEIVED SAMPLE AND ONE ETCHED SAMPLE PER CONDITION AND COMPARISON WITH THE CALCULATED ETCHING DEPTH.

White light interferometry measurements on the remaining cutting marks of the milling process confirm similar etching depths for the etching parameters 150 g/L for 150 s and 300 g/L for 90 s as visible in Figure 3. Compared to the as-received sample in Figure 3, the roughness of etched samples described by Sa (arithmetic mean height) and Sq (the root mean square height) [12] is higher due to pit formation. The pit formation for the condition 250 g/L for 150 s is stronger but more uniformly distributed. Moreover, milling marks are completely removed. The roughness of the samples increases

after 30 days of degradation due to degradation and stronger pit formation. For all 30-day samples no milling marks are visible anymore. Figure 3 shows after degradation that the pits of the as-received sample and the samples with conditions of 150 g/L for 150 s and 250 g/L for 150 s are more homogenously distributed compared to the conditions of 300 g/L for 90 s.
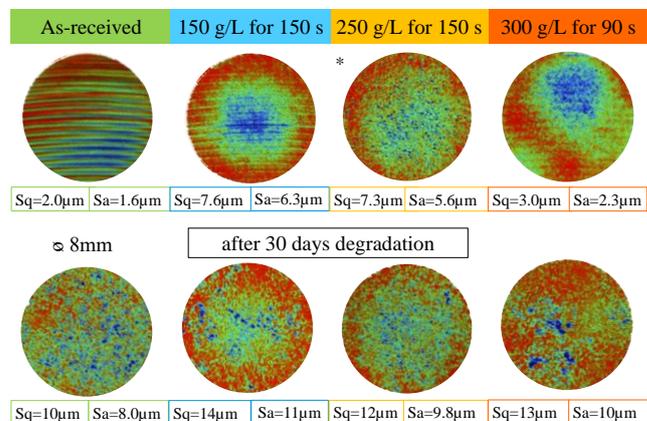

FIGURE 3
3D SURFACE PROFILES OF AS-RECEIVED, ETCHED AND DEGRADED SAMPLES MEASURED BY WHITE LIGHT INTERFEROMETRY (WLI). * MEASUREMENT NOT COMPLETED DUE TO HEIGHT RANGE PROBLEMS, ROUGHNESS VALUES CAN VARY ± 0.7 μm.

Further surface investigations were performed before and after etching with XRD measurements. Figure 4 shows that at a glancing angle of 3° no GdH_2 peaks are detectable for all the as-received samples investigated.
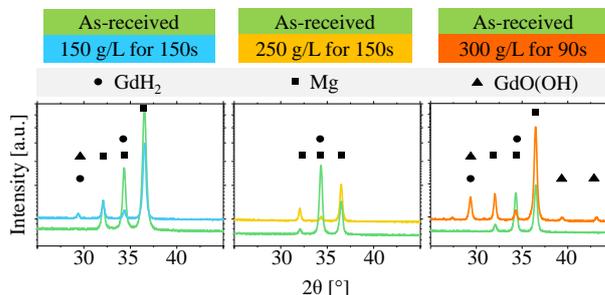

FIGURE 4
XRD PATTERN OF MEASUREMENTS AT A GLANCING ANGLE OF 3° BEFORE (AS-RECEIVED) AND AFTER ETCHING.

After 150 g/L for 150 s etching, the GdH_2 main peak is detectable, which confirms that GdH_2 is formed by etching. After 250 g/L etching, no GdH_2 is found in these samples. Therefore, it can be assumed that this etching procedure removes material from the surface without producing high amounts of GdH_2. It is visible that after the etching procedure 300 g/L for 90 s Gd rich particles like GdH_2 and GdO(OH) were formed. Gd rich particles within the etching holes were also found by SEM as seen in Figure 5 after 2 days of degradation. Rectangular shaped particles with high amounts of Gd are reported as GdH_2 [13]. However, due to the small sizes of the particles inside the etching holes, it is not possible to distinguish between GdH_2 and GdO(OH) by SEM. Figure 5 shows the difference in the amount of Gd rich particles inside the etching holes of different etching conditions. It is assumed that Gd rich particles are formed

during the etching process inside the holes and that particles already present beforehand are not dissolved by etching and falls into the etching pit.
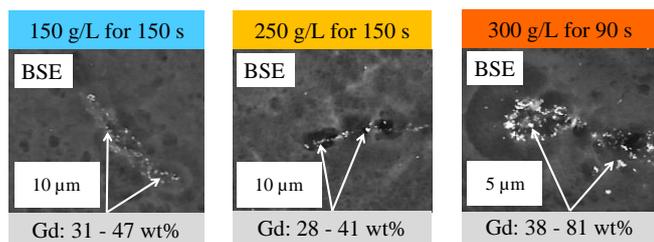

FIGURE 5
SEM/EDX ANALYSIS OF ONE ETCHING PIT AFTER 2 DAYS OF DEGRADATION FOR EVERY CONDITION. GD RICH PARTICLES ARE FOUND ON THE BOTTOM OF THE ETCHING PIT.

In terms of degradation rate, it is visible in Figure 6 that acetic acid etching leads to a reduction of the degradation rate and to a minor scattering of single measurement points. The standard deviation of the mean degradation depth ($\pm$ 0.3 µm) was excluded out of Figure 6 for clarity. For as-received samples the degradation rate amounts to 0.50 µm/day with a non-linear degradation behavior. In comparison, the degradation rate of etched samples amounts to a value of around 0.30 µm/day.
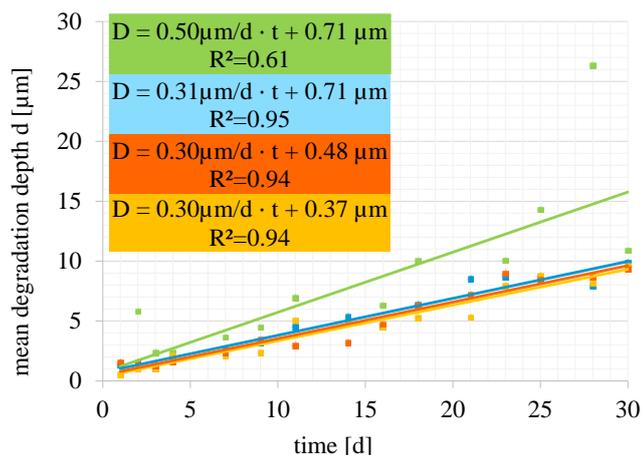

FIGURE 6
GRAPH OF PLOTTED DEGRADATION DEPTH OVER TIME. THE SLOPE OF THE LINEAR FIT IS EQUAL TO THE DEGRADATION RATE.

Due to the fact that all etched conditions lead to a similar linear degradation rate with high linear regression ($R^2 \sim 0.94$), it is assumed that the morphology and roughness after etching does not contribute to the degradation rate. It is reported that twins have an influence on the degradation resistance [9]. Therefore, it is presumed that the removal of the deformation zone, of the high accumulation of twins and of possible impurities permit to avoid differences in electrochemical potential between bulk material and defects in near-surface regions in order to induce a linear degradation. Besides a linear degradation rate, it is also important to sustain a homogeneous degradation. It is supposed that an accumulation of Gd rich particles and remains of accumulated twins can influence a uniform degradation. Additionally, impurities resulting from milling like Fe lead to micro galvanic corrosion and influence the degradation resistance. Further analysis of surfaces with ToF-SIMS, SEM, Interferometry and EBSD are planned to find more differences in microstructure, morphology and impurities between as-received and singly-etched conditions. To investigate the homogeneity of degraded surfaces, further surface analyses are planned, including the analysis of pit volumes, bearing areas and fast Fourier transformation.

4. CONCLUSIONS

• A specific amount of material removal is necessary to avoid different degradation kinetics between deformed grains, twins and the microstructure of the bulk material.
• The etching procedures reduces the scattering of degradation results compared to as-received samples.
• HAc etching of Mg-5Gd represents a good compromise between practicality and effective results in terms of reduction of the degradation rate.
• Accumulation of Gd rich particles and its effects on degradation behavior need further study.

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