Final Draft
of the original manuscript:

Maier, P.; Peters, R.; Mendis, C.L.; Mueller, S.; Hort, N.:
**Influence of Precipitation Hardening in Mg-Y-Nd on Mechanical
and Corrosion Properties**
In: JOM: Journal of the Minerals, Metals and Materials Society (2015)
Springer

DOI: 10.1007/s11837-015-1762-4

Influence of Precipitation Hardening in Mg-Y-Nd on Mechanical and Corrosion Properties

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Abstract

Precipitation hardening is an effective strengthening mechanism to achieve high strength at moderate ductility in Mg-RE alloys. However, improved mechanical properties by precipitates that strengthen the alloy can affect corrosion rates as the finely dispersed particles are often more noble than the matrix. Biodegradable implant material should show a certain corrosion rate, but should be free of pitting, because wide and deep pits are notches that can cause higher stress concentration. WE43 has generally shown an acceptable biological response. In this study, a Mg-Y-Nd-Gd-Dy (WE32) alloy in extruded, solution and precipitation heat-treated conditions has been investigated. Solution heat treatment causes grain growth and strength loss. A rather short ageing response to peak hardness was observed, where peak hardening causes hardness values to exceed that of the initial extruded condition. Grain growth during ageing is not significant. Corrosion was evaluated with potentiodynamic polarization in Ringer Acetate solution. The highest corrosion rate was observed in the T4 condition. The peak aged alloy showed the most homogenous form of corrosion.

1 Introduction

WE43 (Mg-4Y-3RE, where RE is a mixture of rare earth elements) is a high-strength alloy with an acceptable biological response [1]. The hot extruded Mg3Y 1.5Nd0.4Gd0.4Dy (WE32) with a similar composition to WE43 alloy is used in this study. The alloy contains a smaller amount of total alloying additions compared with the commercial WE43.2 Mg-Dy alloys show a uniform corrosion behavior and good cytocompatibility [3–5]. However, Mg-10Dy alloy shows no age-hardening response during ageing, which limits the possibility to tailor properties through heat treatment [6]. Mg-Gd shows a better age-hardening response [7] with similar chemical properties to Dy. Feyerabend et al. [8] described that the acute toxicity of Gd is only moderate. Tests on the cytotoxicity in osteoblast-like cells show that Gd could be a suitable alloying element. WE type alloys are conventionally used in the T6 condition and the intermetallic particles observed in these alloys are fully characterized [9–12] Intermetallic particles $Mg_{12}Nd$ and $Mg_{14}Y_4Nd$ are observed in Mg-Y-Nd and the mechanical properties of the alloy depend strongly on the volume fraction and spatial distribution of these intermetallic phases.

Figure 1: ASTM-G46 standard visual chart for rating of pitting corrosion [13]

This work investigates the influence of the intermetallic particles of an extruded alloy (containing Gd and Dy in addition to Y and Nd) especially on the

corrosion properties: corrosion rate and corrosion morphology. Biomedical applications require an appropriately slow (to avoid strong hydrogen evolution), homogenous corrosion rate. Corrosion pits can cause a reduction in the cross-sectional area resulting in increased mechanical loading and notch effect due to the pits result in increased stress intensity and should be avoided. Where pitting is the predominant form of attack the extent and type of pitting may be evaluated in accordance with ASTM G46-76 [13], see Fig. 1. The wide, shallow pits are least harmful in increasing the stress intensity in a pit compared with narrow sharp pits. Li et al. [14] have shown that the local corrosion behavior and the corrosion rate are strongly dependent on the flow of the electrolyte, and that WE43 is more susceptible to corrosion in a flowing solution. The shear stress applied by the flow promotes local corrosion. Stirring and static tests show lower corrosion rates.

The mechanical properties required for bone implants are still under discussion, but they should maintain mechanical integrity over a time scale of 12–18 weeks while the bone tissue heals and is replaced by natural tissue [1,15]. The allowable strength loss depends on the application itself and is influenced by the bone density and extent of damage on the bone fracture. Thus, the type and extent of corrosion is of an interest for the development of Mg alloys for biomaterial applications.

2 Experimental

The alloys investigated were cast at HelmholtzZentrum Geesthacht under a protective gas mixture of Ar and 2% SF₆ and then hot extruded at the Extrusion Research and Development Center TU Berlin at an overall temperature of 420 °C, a product speed of 2.2 m/min and an extrusion ratio of 37. The overall chemical composition was analysed with inductively coupled plasma–optical emission spectroscopy (ICPOES). The composition of the alloy under investigation is 2.78 wt.% Y, 1.49 wt.% Nd in addition to 0.43 wt.% Gd and 0.41 wt.% Dy. The alloys were solution treated (T4) at 525 °C for 8 h and quenched into warm water at 55 °C to avoid quenching stresses. Based on the literature, [2,10–12] precipitation hardening (T6) was done at 250 °C to achieve appreciable hardening in a relatively short period of time. In accordance with [12], peak ageing was expected within a few hours, so T6 was treated for 2 h, 4 h, 6 h, 8 h and 10 h. To avoid natural ageing, the T6 treatment was carried out within a few hours after T4.

The samples (discs of a diameter of 17 mm) for metallographic and hardness investigations were prepared according to Kree [16] The grain sizes were determined by the line interception method. To evaluate the influence of the heat treatment on corrosion smaller cylinders (overall diameter of 14 mm and height of 10 mm) were used in potentiodynamic polarization, exposed to Ringer-acetate

solution, (where the composition of 1 L of solution contains of 6 g sodium chloride, 3.7 g sodium acetate, 0.134 g calcium chloride, 0.203 g magnesium chloride and 0.4 g potassium chloride), with an initial pH value of 6.5 at a constant temperature of 37 °C (to mimic human body temperature). The potentiodynamic measurements were conducted on samples immediately after grinding with 1200-mesh paper, and cleaning in an ultrasonic bath in ethanol.

A three-electrode flow cell using a counter electrode, an Argenthal reference electrode and a working electrode with a measurement area of $\sim 95 \text{ mm}^2$ (diameter of 11 mm) all in a $\sim 170\text{-mL}$ glass chamber was used to evaluate polarization (current density– potential) curves. Each material condition was tested three times. A flow rate of 8 L/s (overall electrolyte volume was 3.6 L) was used to keep the pH value around 8.5. To force the Mg alloy into strong anodic corrosion, the curve was traced with a scan rate of 50 mV/min from a negative potential of -2000 mV to the positive potential of +4000 mV. The key point of this measurement is to study the passive/transpassive behavior and corrosion morphology of WE32 in three conditions: as-extruded, extruded-T4 and extrudedT6 in peak aged condition. In addition to potentiodynamic polarization, immersion tests were performed: three samples (discs of a diameter of $\sim 15 \text{ mm}$ and a height of $\sim 10 \text{ mm}$) per condition were exposed to 1 L Ringer-Acetate at 37 °C for 7 days. The solution was changed after 4 days. The weight loss was measured without removing the corrosion products and visible changes of the surface were determined.

The tensile properties were measured at room temperature with a TIRA testing machine with an initial speed of 2.4 mm/min. Cylindrical samples with a gauge length of 33 mm and a diameter of 6 mm were used, and up to five samples were tested.

Since tensile tests are not a reliable method for determining the Young's modulus of magnesium, the resonance frequency damping analysis method was used to determine the dynamic modulus of elasticity (DME). Vickers hardness was tested with a universal hardness testing machine ZHU2.5 by Zwick (the sample surface was ground after cutting to reduce residual stresses) with approximately 30 indents per test condition under a load of 1 kg (9.807 N) and the averages are reported.

Samples for transmission electron microscopy (TEM) were prepared by firstly cutting 0.5-mmthick slices with a Streurs Isomat slow speed saw with a diamond blade and grinding to a thickness of $\sim 200 \text{ lm}$. The samples for TEM analysis were prepared by punching 3-mm discs from alloy specimens that were $\sim 200 \text{ }\mu\text{m}$ in thickness and twin jet electropolishing using a solution of 1.5% perchloric acid in methanol at a polishing temperature of -45 °C with a current of $\sim 0.8 \text{ mA}$ to 1.2 mA and a voltage of 50 V. Upon perforation, the specimens were washed in ethanol to remove any trace of acid from them. A Phillips CM200 transmission

Figure 2: Influence of T4 and T6 (2–10 h) heat treatments on hardness and grain size of extruded WE32.

	Extruded	T4	T6-8h
HV1	67.0±2.1	61.0±4.0	77.0±8.1
Grain size (μm)	15.0±7.9	102.0±61.5	99.0±58.9
TYS (MPa)	133.0±3.3	102.5±6.1	133.3±4.7
UTS (MPa)	237.7±0.7	205.7±0.9	235.5±2.7
Elongation (%)	19.2±3.7	18.5±0.7	15.4±2.5
DME (GPa)	44.3±0.2		

Table 1: The tensile properties, hardness and grain size of WE32 in extruded, extruded-T4 and extruded-T6-8 h conditions

electron microscope operating at 200 kV was used for the microstructure characterization.

3 Results and Discussion

In the hot extruded condition, the alloy has a hardness of 67 HV1. Figure 2 and Table 1 show the hardness and average grain size influenced by the heat treatment. The T4 heat-treated alloy containing only supersaturated α -phase shows a lower hardness of 61 HV1 compared to the initial value of 67 HV1, which is explained by the increase in grain size from 15 μm to 102 μm and the dissolution of majority of the intermetallic particles. Following the T4 heat treatment, the alloy was aged at 250 °C for up to 10 h to measure the hardness response over time (T6-2–10 represent T6 heat treatment for 2 h, 4 h, 6 h, 8 h and 10 h). During the age hardening

experiments, the hardness gradually increased from the as-quenched hardness to 77 HV 1 after 8 h. This is slightly longer than the time to peak hardness reported by Kang et al. [12]. No apparent change in the average grain size was observed with T6 heat treatment of up to 10 h at 250 °C.

Figure 3a and b shows microstructural changes during T4. The remaining black spots indicate that not all intermetallic phases are dissolved. Except for Nd, which has a maximum solubility of 3.6 wt.% at the eutectic temperature of 545 °C [17,18] which decreases drastically with decreasing temperature, all other alloying additions in this alloy are significantly lower than their maximum solubility according to their binary phase diagrams. Following ageing at 250 °C for 8 h (peak aged condition), the grain size does not change significantly during ageing (Fig. 3c).

Since hardness measurements provide local mechanical properties and do not give information about the ductility, tensile tests were conducted (regarding T6: only the peak aged condition T6-8 h was tested). Figure 4 and Table 1 show the influence of the heat treatment on strength and ductility. T4 reduces both tensile yield strength (TYS) and ultimate tensile strength (UTS) as a result of the dissolution of most of the intermetallic particles and due to the increased grain size. Elongation at fracture of T4 shows the smallest deviation. T6-8 h increases the ultimate tensile strength back to the initial values of the extruded condition through precipitation; ductility is smaller than that of the T4 heat-treated samples. The yield strength of the T6-8 h heat-treated alloys at 133 MPa is higher than that of the as-extruded alloy at 108 MPa. Macroscopically, cup and cone fracture surfaces were found for extruded WE32.

A more complex failure mode was found for the heat-treated conditions: some samples show a more rugged, shiny ~90° surfaces, others 45° ductile shear fracture characteristics. Fractography images of extruded WE32 reveal typical features of a ductile fracture all over the surface: micro-voids, known as dimples (Fig. 5-a). The fracture surface of the heat-treated condition T4 (see Fig. 5b), being very similar to T6-8 h, shows a mix of ductile features (dimples) accompanied with cleavage fracture parts in rather larger grains. The ultimate tensile strength values do not exceed that of the extruded condition. However, the tensile yield strength of the peak aged material is higher than that observed in the initial extruded material. The explanation for the difference in hardness and ultimate tensile strength is as follows.

It is assumed that during ageing the maximum grain size increases. The average (mean) values and standard deviation do not show the complete picture. According to Fig. 2, these values do not change significantly. However, looking at the grain size distribution in the histograms in Fig. 6, the number of small and large grains increase with ageing (see T6-8 h). The distribution of grain sizes changes from a standard normal (T4) into a less bell-shaped, more bimodal dis-

Figure 3: Microstructure of extruded WE32: (a) extruded, (b) extrudedT4 and (c) extruded-T6-8 h (peak aged condition).

Figure 4: AInfluence of heat treatment T4 and T6-8 h (peak aged condition) on tensile properties of extruded WE32.

	Extruded	T4	T6-8h
Current density range I (mA/cm ²)	17-25	18-31	18-25
Potential E breakdown (mV)	-	2200	3200
Corroded cross section area (mm ²)	5.44 ± 0.39	5.99 ± 0.70	5.22 ± 0.28

Table 2: Corrosion properties of WE32: extruded, extruded-T4 and extruded-T6-8 h

tribution (T6-8 h). In tensile tests, the material fails at the weakest link, being the larger grains. It seems that ageing also leads to the formation of smaller grains. This could be a result of discontinuous grain growth, where certain grains grow rapidly in a matrix of finer grains resulting in a bimodal grain size distribution. The presence of solid-state precipitates hinders the dislocation slip increasing the yield strength. At the yielding, there is a high density of dislocations which lead to a high degree of plasticity and result in lower work hardening and negligible increase in the ultimate tensile strength. The higher density of dislocations forming due to the increase in the yield strength presents an increased density of defects at a given strain and results in a reduced elongation to failure.

The mechanical properties can be adjusted by precipitation hardening. In biomedical applications, the corrosion rate and morphology are also of interest. Figure 7a–c (single curves), Fig. 8 (overview) and Table 2 show the influence of heat treatment on corrosion behavior, evaluated with potentiodynamic polarization, from -2000 mV to +4000 mV. The fine-grained extruded material has a

Figure 5: SEM fractography images of WE32 tensile samples: (a) extruded and (b) after extruded-T4 heat treatment.

Figure 6: Grain size distribution by histograms of extruded WE32 in extruded-T4 (top) and extruded-T6-8 h (bottom).

current density at around 20 mA/cm² with range of values between 17 and 25 mA/cm² up to 2300 mV, where the curve shows larger variations in current density. However, there is no visible breakdown potential. The T4 condition shows the highest range of current density values, reaching from 18 to 31 mA/cm². Following a potential of 2200 mV, the current density increases significantly, indicating a breakdown potential. The peak aged condition shows a breakdown potential at 3200 mV and up to this value the current density ranges between 18 and 25 mA/cm². Below a potential of 1500 mV, the curves of the T6-8 h condition show the least deviations in current density.

Figure 8 presents in an overview where the influence of heat treatment on potentiodynamic polarization is observed: T4 shows the highest corrosion rate indicated by the highest current density. As described above, the extruded and the T6-8 h conditions show very similar corrosion behavior until the breakdown potential was reached for the T6-8 h condition at 3200 mV.

Another approach to determine the extent of corrosion is to measure the corroded area from the cross-section of the corroded sample. The samples were ground through the cross-section of the cylinder without removing the corrosion product. Since only the inner region of the cylinder face was corroded, the initial surface (an outer ring of 1.5 mm) could be used as a reference. Figure 9a–c

Figure 7: Influence of heat treatment on corrosion measured with potentiodynamic polarization of extruded WE32: (a) extruded, (b) extruded-T4 and (c) extruded-T6-8 h, single curves.

Figure 8: Overview of heat treatment on corrosion by potentiodynamic polarization of WE32 in extruded, extruded-T4 and extruded-T6-8 h condition.

Figure 9: Cross-sectional macrographs showing corrosion morphology and corroded area of extruded WE32: (a) extruded, (b) extruded-T4 and (c) extruded-T6-8 h.

shows representative corroded areas of the crosssection (cutting the cylinder in half lengthwise) and some corrosion depths are given (compare the current density range values in Table 2). The most homogenous corrosion morphology is observed in the T6-8 h condition, i.e. shallowest corrosion pits (compare Fig. 10a–c).

Table 2 summarizes the results from the potentiodynamic polarization tests (I and E values taken from Figs. 7 and 8) as well as the area of the corroded cross-sections after the potentiodynamic measurement reached 4000 mV. The highest corrosion rate (see highest current density) of the T4 condition agrees with the highest corroded area. Comparing the extruded and T6-8 h conditions, no relationship between current density and corroded area appears: extruded material shows a higher corroded cross-section area with only a marginally higher range in current density values. Current density bursts within the passive part of the potential–current density curve is an indicator of alternating breakdown and repassivation (current bursts). Polarization curves indicate this with a metastable pitting region (pit initiation followed by repassivation) prior to the formation of pits which develop at breakdown potential, also often called pitting potential, corresponding to findings in steel [19] and titanium [20]. As previously mentioned, there are only a few current bursts in the polarization curves of the T6-8 h condition, at least below 1500 mV, thus lower density of pits are expected.

To underline the differences in corrosion morphology, cross-sectional micrographs are used to describe the type of pitting and show a higher resistance to pitting corrosion in the peak aged condition T6-8 h. Figure 10a (extruded) and b (T4) shows examples of elliptical and undercutting pits (see arrows) observed at the end of the potentiodynamic measurement. In the T6-8 h condition, the pits are wider and shallow, which are less harmful. These micrographs show the results expected from the polarization curves. However, the stage at which these pits form and how they grow cannot be determined from these micrographs. In our current research, polarization tests are used to measure the potentiodynamic curves to a lower potential value (500 mV). This will remove the last stage effects due to pitting corrosion and will compare only the general corrosion.

After the immersion tests, only the T6-8 h condition still shows a weight increase by a small amount, $\sim 1.3\%$ (the lowest amount of corrosion products have been found in the glass cylinder). The surfaces of the discs of the T6-8 h samples were not completely covered with corrosion products. Extruded material and condition T4 show weight loss: down to $\sim 97\%$ and $\sim 89\%$ of the starting mass. The surfaces are completely covered with corrosion products. These results agree with the potentiodynamic polarization tests (compare Table II): The extruded and T4 condition behave similarly during immersion tests (both show weight loss), with T6-8 h showing the lowest corrosion rate.

Figure 10: Cross-sectional micrographs showing corrosion morphology of extruded WE32: (a) extruded, (b) extruded-T4 and (c) extruded-T6-8 h.

Figure 11: TEM images and EDX-spectra of extruded WE32: (a) extruded, (b) EDX-spectra of intermetallic phase in (a), (c) extruded-T4 (electron beam direction parallel to $\langle 11\bar{2}0 \rangle$) and (d) extruded-T6-8 h (electron beam direction parallel to $[0001]$).

Since both microgalvanic corrosion and precipitate strengthening are mostly influenced by the type and morphology of the precipitate, its volume fraction and spatial distribution, so transmission electron microscopy (TEM) images and EDX have been used to give more details on this. From the binary and ternary phase diagrams and according to [21], β -precipitates such as Mg_3Nd , Mg_{24}Y_5 , $\text{Mg}_{24}\text{Dy}_5$, Mg_5Gd and $\text{Mg}_{14}\text{Y}_4\text{Nd}$ can form. Figure 11a–d shows TEM images of the three material conditions investigated. The intermetallic phases found in the extruded condition (Fig. 11a) suggest a stoichiometry of $\text{Mg}_5(\text{Gd,Y,Dy,Nd})$, see Fig. 11b.

The analysis of the diffraction patterns (not shown here) may be index similar to the Mg_5Gd phase. Apps et al. [22] reported that in Mg-7Gd-2Nd alloy the Nd:Gd ratio is close to 1:1 in the intermetallic phases, suggesting a stoichiometry of $\text{Mg}_5(\text{Nd}_{0.5}\text{Gd}_{0.5})$. In Mg-7Dy-2Nd alloy, the Nd concentration is significantly higher than that of Dy, suggesting a stoichiometry near $\text{Mg}_5(\text{Nd}_{0.7}\text{Dy}_{0.3})$. In Mg-4Y-2Nd alloy, the Nd:Y ratio is close to 1:2, suggesting a stoichiometry near $\text{Mg}_5(\text{Nd}_{0.33}\text{Y}_{0.67})$. The stoichiometry of the intermetallic phases reported in previous investigations are similar to that observed in this investigation.

Even when the material is quenched in warm water after solution heat treatment, a certain amount of dislocations can be found (see white and black arrows in Fig. 11c). The increased density of dislocations is due to coalescence of mobile quenched in vacancies immediately after warm water quenching. There are no precipitates observed following T4 heat treatment. The dislocation density found in the T4 heat-treated material is too low for the formation of sub-grains and the subsequent recrystallization. However, the number of larger grains and the grain size itself increased.

Taking a look back at Fig. 2, the mean grain size does not change, so it is always recommended to check the grain size distribution. This is especially important for the mechanical properties: large grains are weak points where strength and brittleness are concerned. Figure 11d shows fine dispersed precipitates in the peak aged condition, which is responsible for the precipitation hardening. The fine precipitates observed in the T6-8 h condition change the surface morphology to a more homogenous corrosion, with fewer undercutting pits and decreased corrosion rate compared with extruded and T4 heat-treated conditions.

4 Summary

This study has shown that precipitation hardening in a $\text{Mg3Y1.5Nd0.4Gd0.4Dy}$ (WE32) alloy is an effective mechanism to strengthen the material as well as to modify the corrosion morphology by changing the amount and size of second phases.

A short ageing time of 8 h at 250 °C is observed for peak hardness. This peak hardening causes hardness values exceeding the initial extruded condition by 15% and tensile yield strength by 23%. This peak hardening reduces ductility to 80% of that reported for the extruded alloy, which is due to grain size growth from 15 μm to 100 μm .

Grain growth during ageing is not as significant as the increase in grain size during the solution heat treatment.

The corrosion behavior in Ringer-Acetate solution was evaluated, using potentiodynamic polarization and by immersion testing to evaluate corrosion morphology and the corroded area using cross-section micrographs. The highest corrosion rate was found following the T4 heat treatment, and both approaches provide similar results: the highest corroded area correlates with the highest current density. The range of current density values are similar between the extruded and the peak aged T6-8 h conditions. However, the extruded condition shows larger corroded areas. This agrees with the appearance of current bursts indicating breakdown and repassivation, hence stronger corrosion. The peak aged alloy shows the smoothest current density potential curve before breakdown, resulting in the most homogeneous corrosion.

A fine dispersion of precipitates through optimized precipitation hardening is suggested for a homogeneous corrosion morphology. However, alloy and process design should aim to keep the grain size as small as possible. A slight increase in alloying composition may be the way forward.

Acknowledgments

The authors acknowledge the support of Felix Worschech and Hartmut Habeck from UAS Stralsund. Martin Wolff (HZG) is acknowledged for measuring the dynamic modulus of elasticity.

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