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Cyclic deformation of newly developed Magnesium cast alloys in corrosive environment

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Abstract The moderate corrosion rate exhibits by Mg-RE alloys make it candidate material for biodegradable implant. Owing to the operating environment, implants are subjected to stochastic cyclic load and chemical condition. The alloys response to the subjected condition determines its degree of applicability. This work studies the cyclic deformation of newly developed Mg10GdxNd alloys both in air and under corrosive environment. The corrosion fatigue test was carried out in Ringer-Acetate solution and was evaluated using mechanical hysteresis and pH-value measurements. The microstructural changes in correlation to the deformation parameters and fracture surfaces were characterized using SEM. Results show that alloying Mg10Gd with Neodymium improved its fatigue live both in air and corrosive medium. Chilled casted Mg10Gd and Mg10GdxNd were found to undergo brittle fracture in both media. Loading in Ringer-Acetate was found to reduce the fatigue life of the investigated alloys due to the interaction of corrosion and fatigue processes on the microstructure of the alloys. EDX analysis suggests that the improved fatigue life observed on the Mg10GdxNd is connected to the new ternary Mg-Gd-Nd phase observed in the microstructure.

Introduction

Most of the research activities in the past on Mg alloys focused on improving the corrosion and mechanical properties of these alloys for structural application [1]. The current state of knowledge however shows that the corrosion of Mg and its alloys could be taken advantage of to design adequate biodegradable human bone implant [2]-[6]. Effective Mg alloy implant is expected to corrode reasonably while providing the mechanical support that is necessary for the healing process of the bones. The effectiveness of the mechanical response of the Mg-alloy implant depends strongly on the corrosion rate, which in turn depends on the alloying elements, processing route and the implant environment [7]. Previous works show that Gadolinium (Gd) addition reduces the corrosion rate of Mg and improves its strength while reducing the elongation to fracture [8],[9]. The work of reference [8] illustrated that Mg10Gd has the best corrosion property in comparison to Mg2Gd, Mg5Gd and Mg15Gd alloys investigated. However, the fatigue behaviors of this potential Mg-RE implant have not been thoroughly studied. In this work, a third rare earth element Nd was added to Mg10Gd and its cyclic deformation response studied under air and corrosive media. Preliminary result show that the fatigue live of Mg10Gd was improved by up to 19 % and 31 % by addition of 1 wt.% and 2 wt. % of Nd respectively. Mg10Gd2Nd shows more noble behavior in Ringer-Acetate solution than Mg10Gd1Nd while maintaining also longer fatigue life in the corrosive medium.

Experimental Procedures

Fatigue and corrosion fatigue test were carried out on permanent mould direct chill cast Mg10Gd, Mg10Gd1Nd and Mg10Gd2Nd produced at Helmholtz Centre Geesthacht. Round samples (diameter of 6mm) were machined with surface roughness of 6.3 µm. Fatigue and corrosion fatigue test were performed on a closed-loop servo hydraulic testing machine system MTS820. Test were carried out in stress controlled mode using constant load with a stress ratio of R = -1 and a frequency of 5 Hz. Measurements were limited to $2*10^6$ cycles while Ringer-Acetate solution was used as the corrosive media in the corrosion fatigue test. A voltametric cell was used to evaluate the free corrosion potential (open Circuit Potential - OCP- R10/R12) and passivity. The OCP and the current density - potential curve were measured using an Argenthal reference electrode. The microstructure and fracture surfaces of the investigated alloys were characterized using a Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-ray Spectroscopy (EDX) for chemical analysis. Tensile and compression test was carried out according to EN 10002-1:2001 standard.

Results and Discussions

Fatigue test: Fig. 1(a,b) show the S-N curve of Mg10Gd and Mg10Gd2Nd (fatigue limit of $2*10^6$ cycles. Mg10Gd shows fatigue strength of 52 MPa while Mg10Gd2Nd 68 MPa respectively (Mg10Gd1Nd 62 MPa, not shown). Grey lines indicate the probability of failure from 0 to 100 %. Fig. 1(c) shows the SEM fractured surface of Mg10Gd1Nd and indicates a brittle fracture (elongation to fracture in tensile test less than 2 %). The same tendency of increase in strength was also observed in both tensile and compression test with the addition of Nd on the Mg10Gd alloy. Whereas Mg10Gd shows yield strength of 60 MPa, Mg10Gd1Nd and Mg10Gd2Nd show that of 75 MPa and 97 MPa in tensile mode. The compressive yield strength shows the same trend with Mg10Gd having 76 MPa while Mg10Gd1Nd and Mg10Gd2Nd were 121 MPa and 123 MPa respectively.

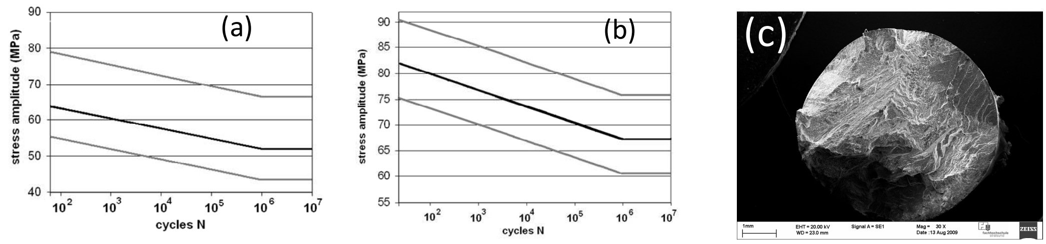

Fig. 1: S-N curve of (a) Mg10Gd, (b) Mg10Gd2Nd and (c) SEM micrograph of Mg10Gd1Nd

This increase in fatigue strength is as a result of the formation of Mg-Gd phase which are rich in Nd. Previous investigation shows that the eutectic Mg_5Gd are observed in Mg alloy with more than 2 wt. % Gd mostly at the grain boundary regions [8]. These micrometer scale precipitates are dissolved in T4 condition and reappears as metastable β′ and β″ precipitates after T6 heat treatment [8]. In another work (Mg-11Gd-2Nd-0.5Zr), the eutectic phase was characterized to be of Mg_5Gd prototype with stoichiometry near the $Mg_5Nd_xGd_{1-x}$($x \approx 0.43$) [10]. Reference [11] while characterizing Mg-7Gd-2.25Nd suggests that the eutectic phase has an FCC crystal structure (a≈2.2 nm) and stoichiometry near $Mg_5(Nd_{0.5}Gd_{0.5})$. This Mg-Gd-Nd ternary phase is responsible for the improved fatigue strength observed in the Nd containing Mg10Gd alloys; even when no heat treatment has been done. During fatigue test, the cyclic deformation behavior of the alloys were monitored by evaluating the movement (cyclic creep) and change in shape (material strengthening/ softening) of the hysteresis loop based on the number of cycles. Fig. 2 represents the cyclic deformation behavior of Mg10Gd2Nd subjected to 80 MPa stress resulting at 10,900 cycles to fracture. The total strain decreases up to 2,000 cycles, stays relatively constant at 10,000 cycles and increases strongly just before fracture. This corresponds to material strengthening at the inception of cyclic deformation and material softening within the last cycles. As observed in Fig. 2, the hysteresis loop shift to the right is typical of cyclic tensile creep. Due to twinning, Mg-alloys usually show compressive cyclic creep [12]. However, alloying with RE elements seems to change the behavior to cyclic tensile creep [13].

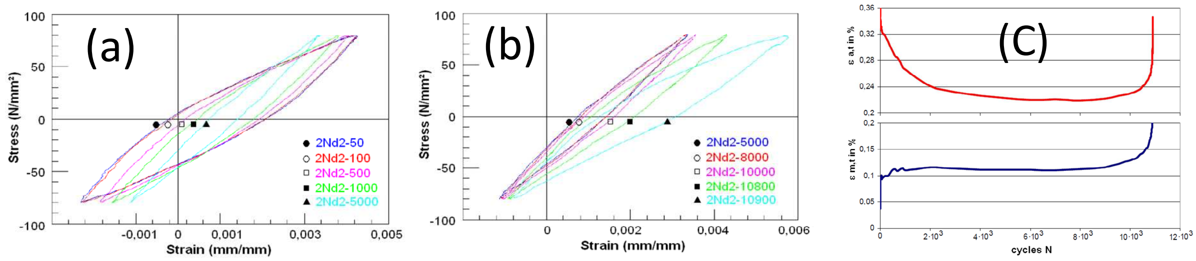

Fig. 2: Mg10Gd2Nd: (a-b) Hysteresis loop development, (c) Strain change and cyclic creep

Corrosion test: Figure 3 represent the corrosion behavior of the alloys in Ringer-Acetate solution. The OCP measurement shows that Mg10Gd reaches its free potential after 300 sec., followed by Mg10Gd2Nd after 900 sec. with a similar value. OCP shifts towards noble potential due to passivation. However, Mg10Gd1Nd reaches saturation very slowly and OCP shows a lower value. OCP after voltametric measurements shows the same order of free potential; 1%Nd presents the less noble alloy. The current density - voltage curves (i-E curves) show that alloying 2%Nd has the strongest tendency to form a passivity layer and shifts the equilibrium and breakdown potential furthest to the right, irrespective of the grain mesh. The potential values of Mg10Gd and Mg10Gd1Nd vary much with respect to grain mesh, as observed in figure 3. It also can be seen that using 1200 grain mesh increases the potential values generally. Considering the Ringer-Acetate solution used in this work, Mg10Gd2Nd shows more noble response. It is likely that the behavioral pattern may change in a different electrolyte as the alloying elements reacts differently with respect to varied corrosive medium. However, bone implant materials are expect to corrode homogeneously while maintaining the necessary mechanical support needed within the healing duration [2].

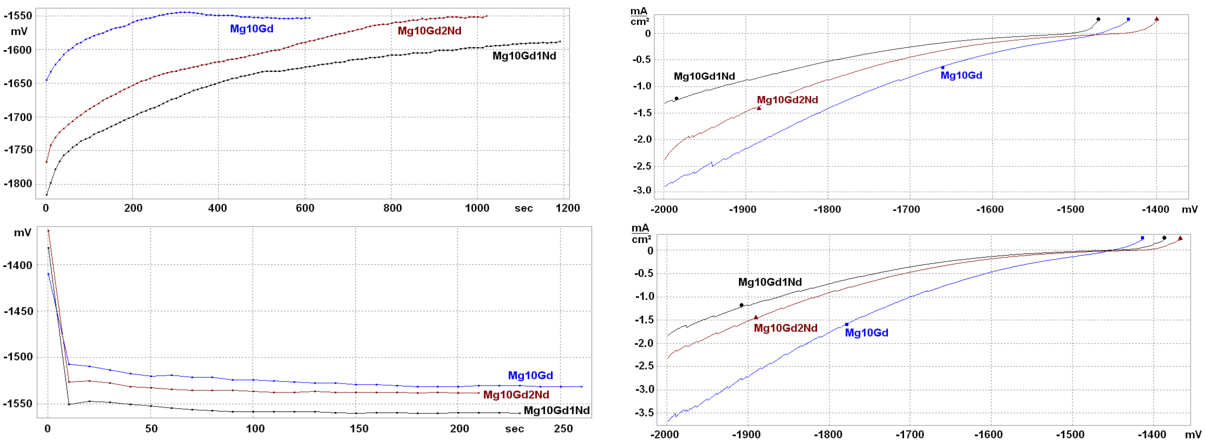

Fig. 3: 1200 grain mesh: OCP R10 (top left) and OCP R12 (bottom left). Voltametric i-E curve at 500 grain mesh (top right) and 1200 grain mesh (bottom right) at room temperature

Fatigue corrosion test: Fig. 4 (a) shows the development of selective corrosion (developing into pitting corrosion) on the surface of the sample in the fatigue corrosion chamber while Fig. 4 (b) shows the fractured sample with corrosion products. Fig. 4 (c) shows the fractured surface. What is obvious is that, the numbers of cycles to fracture are reduced considerably due to Ringer-Acetate solution. Again, Mg10Gd2Nd sustained higher cycles to fracture than Mg10Gd1Nd in this corrosive medium. For stresses of 60 MPa and 50 MPa, Mg10Gd1Nd fractured after 26,000 and 270, 000 cycles respectively. Mg10Gd2Nd fractured after 140,000 and 280,000 cycles respectively. EDX analysis on the fractured surface shows that corrosion products consists of high percentage of oxygen and chlorine, lower amount of RE elements were observed. Pitting corrosion areas act as crack tip during fatigue test and thus strongly reducing the number of cycles to fracture. During corrosion fatigue test, the pH values increased from between 7 and 7.5 at the inception of the test to 10.5 after 200,000 cycles. Previous work suggested that an accelerated corrosion of Mg-alloy implant could be expected in vivo as the local pH was estimated at 7.4 or lower due to secondary acidosis resulting from metabolic and resorptive processes after surgery [14]. Another work shows that pH value (> 11.5) will promote a stable protective hydroxide layer on the surface of the Mg-alloy implant while less than 11.5 will facilitate corrosion of the Mg-alloy in corrosive medium [15]. An observation of Fig. 4(b) show however a uniform corrosion attack on Mg10Gd2Nd.

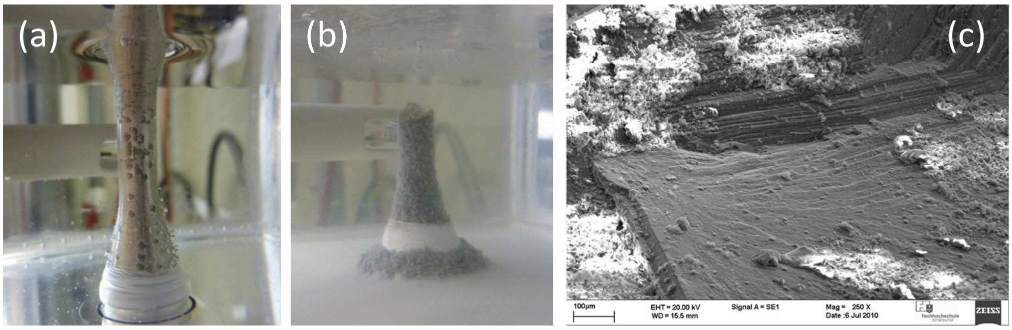

Fig. 4: (a) Development of pitting corrosion, (b) fractured sample with corrosion product and (c) fractured surface of the Mg10Gd1Nd (area close to the tip initiation)

Conclusions

Addition of Nd to Mg10Gd show improved fatigue strength both in air and in Ringer-Acetate solution. Mg10Gd2Nd exhibited nobler characteristic (OCP) with respect to Mg10Gd1Nd and Mg10Gd and also shows a higher equilibrium and breakdown potential. The improved properties observed in this Nd modified alloy are connected with the Mg-Gd phase rich in Nd. This could be a potential implant material with further development, however in vivo experiments are necessary to gain more insight into this Nd modified Mg-Gd alloy.

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References

[1] E. F. Emley: Principles of Magnesium Technology (Pergamon Press, Oxford 1966)
[2] F. Witte et al.: Biomaterials 27 (2006), p. 1013-1018
[3] F. Feyerabend et al.: Acta Biomaterialia 6 (2010), p. 1834-1842
[4] L. P. Xu et al.: Journal of Biomed Mater. Research 83A (2007), p. 703-711
[5] F. Witte et al.: Current Opinion in Solid State and Material Science 12 (2008), p.63-72
[6] G. D. Zhang et al.: Acta Metall 43 (2007), p. 1186-1190
[7] H. K. Toenshoff et al.: Materialwiss Werkstofftechnik 32 (1) (2001), p. 62-67
[8] N. Hort et al.: Acta Biomaterialia 6 (2010), p. 1714-1725
[9] L. L. Rokhlin: Magnesium alloys containing rare earth elements–structure and properties (Taylor & Francis, London 2003)
[10] K. Zheng et al.: Magnesium Technology 2008, edited by M. O. Pekguleryuz et al.
[11] P. J. Apps et al.: ScriptaMater. 48 (2007), p. 475-481
[12] S.M Yin et al.: Scripta Materialia 58 (2008), p. 751-754
[13] P. Maier and C, Fleck.: Proceedings of the Eurocorr (2007), Freiburg, Germany
[14] F. Witte et al.: Biomaterials 26 (2005), p. 3557-3563
[15] M. Pourbaix: Atlas of Electrochemical equilibria in aqueous solutions (National Association of Corrosion Engineers, Houston, 1974)