

# MODELLING OF BIOMATERIALS PROPERTIES MAGNESIUM-BASED ALLOYS

PANDA ANTON<sup>1</sup>, DYADYURA KOSTIANTYN<sup>2</sup>

<sup>1</sup>Technical University of Kosice  
Faculty of Manufacturing Technologies with a seat in Presov,  
Department of Manufacturing Technologies, Slovak Republic

<sup>2</sup>Sumy State University, Faculty of Technical Systems and  
Energy Efficient Technologies, Sumy, Ukraine

DOI: 10.17973/MMSJ.2017\_12\_201739

e-mail: [anton.panda@tuke.sk](mailto:anton.panda@tuke.sk)

The degradation behavior of magnesium-based alloys is obviously important for medical applications of biomaterials. Magnesium alloys were investigated as implant materials. This article critically summarizes the in vivo knowledge and experience that has been reported on the use of magnesium and its alloys to advance the field of biodegradable metals. The efficiency of the development approach is discussed. Thermo-physical and physical properties of liquid and solid phases during solidification are critical data for simulations. However, the number of alloys for which such information is available is limited, primarily due to the difficulty in experimentally determining these properties during the casting/solidification process. This article will focus on demonstrate the value of integrating the modelling of solidification and the associated. This include show changes in the composition of an magnesium alloys within its specification range can substantially affect its properties during solidification and how properties of the liquid can vary significantly in the mushy zone.

## KEYWORDS

modelling, magnesium alloys, magnesium composite, biocompatibility, in vitro and in vivo corrosion, biomaterials, orthopaedics, biodegradable metallic implants.

## 1 INTRODUCTION

Biomaterial implants can either be used to replace a diseased part or to assist in the healing process. The latter application only requires that the implant remain in the body temporarily. In situations where a permanent implant is used for a temporary application, additional surgeries are required to remove these devices once the healing process is complete. This removal process increases the cost and patient morbidity. In contrast, biodegradable materials dissolve after the healing process is complete and thus, no additional surgeries are required for removal of these implants. This also eliminates the complications associated with the long-term presence of implants in the body. Lastly, once these materials degrade within the body, it is important that the degradation products are able to be metabolized by the body, and thus bioabsorbable. Biologically, the material and substances released during degradation must not be harmful to the human body. [Purnama A. 2010, StJohn D.H. 2005]

Magnesium shows great promise as a potential biocompatible and biodegradable material [Janz A. 2007, Janz A. 2009, Yang S. 2011]. Magnesium (Mg) and its alloys have been advocated as

potential candidates to serve this purpose for obvious reasons. The density (1.74 g/cm<sup>3</sup>) and Young's modulus (42 GPa) of Mg are much closer to those of bone than stainless steels or Ti alloys. However, the rapid degradation in the physiological environment hampers its clinical use. Therefore, one of the most exigent problems concerning Mg and Mg alloys is the unpredictable corrosion behavior in vivo, where numerous ions are present in the body fluids (e.g. Na, K, Ca, Mg, HCO<sub>3</sub>, Cl, HPO<sub>4</sub> and SO<sub>4</sub>) that make metallic corrosion very hard to predict or define. Thus, to compensate or even improve the antimicrobial activity of the Mg alloy, the elements having antimicrobial property should be chosen as alloy or coating compositions to enhance the corrosion resistance of Mg alloy. [Pandova 2014, Pandova 2016, Zaborowski 2007] To reduce the degradation rate of Mg to match the bone union, alloying and surface coating have been used. But, high corrosion resistance of Mg alloys results in a low alkaline pH, which will compromise the antibacterial activity because the antibacterial property of Mg is attributed to and proportional to the alkaline pH, which increases with Mg corrosion. [Seitz 2014, Zhao 2015, Lock. 2014]

The properties are of great importance as high mechanical strength reduces the amount of implant material needed for a given applied load and reducing the elastic modulus mismatch alleviates stress-shielding effects between bone and the implant material.

A substantial number of scientific publications regarding the degradation of Mg and its alloys have reported a large range of results due to the different materials, methods and experimental conditions selected. To the best of our knowledge there has not been a systematic approach, or agreement on the experimental conditions necessary.

In the following we present the design strategy employed for the development of high strength Mg alloys for degradable implant applications in osteosynthesis. 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. [Zhao 2015, Panda 2013, Mordike 2001]

## 2 GENERAL: MAJOR RECENT ADVANCES

### 2.1 Magnesium alloys

The magnesium alloys currently under investigation as implant materials are mostly commercial alloys which have been developed for the needs in transportation industry [ASTM B296-03. 2014]. The designation system of magnesium alloys is generally following the nomenclature of the American Society for Testing and Materials (ASTM). The magnesium alloys can be divided into three major groups: pure magnesium (Mg) with traces of other elements, aluminium (Al) containing alloys and those alloys which are free of Al. Typical Al containing magnesium alloys are AZ91, AZ31, AE21, calcium (Ca) modified AZ alloys, and LAE442. AZ31 and AZ91 have been used over

decades in technical applications [Luo 2012b, Berglund 2012, Zhang 2014]. Aluminum (Al) is a major alloying element in Mg-based alloys and is considered to enhance the strength and corrosion resistance. However, it has poor biocompatibility, which causes phosphate depletion in tissues and lowers phosphate absorption from digestive tract.

Calcium and Zn are two essential elements in human body that also provide mechanical strengthening in Mg-based alloys. Calcium has been reported to improve the corrosion resistance of Mg-based alloys in simulated body fluid. Zn, one of the essential elements in the human body, has been proved to have antibacterial effects. Meanwhile, Zn additions increase the strength of Mg-based alloys primarily through to precipitation strengthening. A slower degradation rate of Mg alloys is required in order to give time for the body to regulate the OH- and H<sub>2</sub> gas that might be generated during degradation. In addition to the given elements Al and zinc (Zn), these alloys also contain a small amount of manganese (Mn).

AE21 consists of Mg, Al, rare earth elements (RE), a small amount of Mn. Furthermore, its composition is very similar to the commercial creep resistant alloy AE42. LAE442 is based on the alloy AE42 and contains Al, RE, Mn and additionally lithium (Li). LAE442 has been developed recently as a density reduced magnesium alloy with improved ductility and enhanced corrosion properties. Typical Al-free magnesium alloy systems are WE, MZ, WZ, and Mg–Ca alloys. The magnesium alloy WE43 has been developed to improve creep resistance and high temperature stability. This alloy contains yttrium (Y), zirconium (Zr) and RE respectively. Zr has also been reported to have antibacterial properties. Manganese–zinc (MZ) alloys have comparable properties to the alloying system ZM, which is a known system for wrought applications in the transportation industry. However, almost none of the above mentioned alloys have been originally developed to be a biodegradable implant material. Due to the complex alloy composition it is not certain, if the observed in vivo degradation can be truly connected to a chemical element, an intermetallic compound or a microstructural effect based on the processing route.

In addition, 23 thermodynamic descriptions for ternary systems have been developed and are implemented in the Mg database, classified with status B and unpublished. These are 8 Mg-systems: Mg–Al–Y, Mg–Cu–Ni, Mg–Gd–Mn, Mg–Li–Zn, Mg–Mn–Y, Mg–Mn–Zr, Mg–Ni–Si, Mg–Y–Zr; and 15 non-Mg systems: Al–Ca–Ce, Al–Ca–Li, Al–Ca–Si, Al–Ce–Gd, Al–Ce–La, Al–Ce–Y, Al–Cu–Nd, Al–Gd–La, Al–Gd–Nd, Al–Gd–Y, Al–La–Nd, Al–La–Y, Al–Li–Mn, Al–Mn–Sc, Cu–Ni–Si.

Thermodynamic descriptions of intermetallic solution phases should be guided by their crystal structure. Generally, such phases occurring in different binary systems may be modeled as the same phase if they share the same crystal structure. Joining such phases enables more realistic predictions of multicomponent alloy phase diagrams and phase formation calculations. The diversity of such unified phases is emphasized. On the basis of meticulous Calphad modeling of the binary and ternary systems and consistent treatment of multicomponent intermetallic solution phases, the following rule of thumb is proper for Mg alloy thermodynamics: The more components that are included, the less additional information is required. That enables applications of truly multicomponent Mg alloys involving thermodynamic calculation of any kind of phase diagram sections or liquidus and solidus projections, solidification simulation using the limiting Scheil and equilibrium conditions and obtaining thermodynamic driving forces for kinetic processes. [Song 2007, Luo 2012a, Luo 2012b, Berglund 2012, Zhang 2014, Novakova-Marcincinova 2014b, Cao 2006, Sun 2012, Rad 2012, Panda 2016b]

## 2.2 The effect of alloying elements

Alongside pure magnesium, the chemical elements Al, Mn, Zn, Ca, Li, Zr, Y and RE are used in magnesium implant materials. The detailed metallurgical and metal physical reasons for their use are described in. In general, these elements influence the mechanical and physical properties of magnesium alloys in industrial applications. Most of the given alloying elements can react with magnesium or among each other to form intermetallic phases. These phases contribute to enhance the alloy's strength by precipitation strengthening. Both solid solution strengthening and precipitation strengthening improve strength, but deteriorate the alloy's ductility. However, almost any alloying element contributes to some extent to grain refinement which serves as a strengthening mechanism known as grain boundary strengthening or Hall–Petch strengthening. Grain boundary strengthening improves both strength and ductility. Characteristic impurities in magnesium alloys are iron (Fe), copper (Cu), nickel (Ni), and beryllium (Be). The amount of impurities depends on the alloy's composition, the technology for production and the progress in alloy development. Typically, Be is limited to 4 ppm. The amount of Cu is limited normally to 100–300 ppm, Fe to 35–50 ppm, and Ni should not exceed 20–50 ppm. Other chemical elements are referred as normal alloying elements and their limits are given together with the nominal contents of alloying elements. For biomedical applications, the amount of these impurities has to be strictly controlled. Although the given impurity concentrations are low compared to the physiological range in the body, elements such as beryllium and nickel should be avoided. In general, the amount of impurities should be kept minimal, supporting the aim to obtain more comparable and standardized magnesium alloys.

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. that in addition is particularly tolerant of slight deviations in composition while maintaining the overall performance.

[Friedrich 2006, Novakova-Marcincinova 2013, Schmid-Fetzer 2012, Rad 2012, Koike 2003b, Wu 2002, Panda 2016b]

## 2.3 Microstructural and mechanical performance

Grain refinement of Mg alloys is a well known and efficient approach for enhancing both the strength and the ductility of the material [StJohn 2005]. Upon grain refinement, the strength of an alloy is heightened by grain boundary hardening described by the Hall–Petch relationship [Purnama 2010], and the ductility is increased due to an activation of non-basal slip deformation modes based on compatibility stresses near grain boundaries [Koike 2003a, Koike 2003b].

The relation between yield stress and grain size is described mathematically by the Hall–Petch equation:

$$\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}} \quad (1)$$

where  $\sigma_y$  is the yield stress,  $\sigma_0$  is a materials constant for the starting stress for dislocation movement (or the resistance of the lattice to dislocation motion),  $k_y$  is the strengthening coefficient (a constant specific to each material), and  $d$  is the average grain diameter.

Evaluation of the mechanical properties by tensile and compressive testing shows a good combination of strength and ductility for alloys in all states (as-extruded and heat-treated). Moreover, the tests reveal that the appropriate choice of heat treatment parameters enables controlling the alloys stress–strain performance. The attractive mechanical properties of the

alloys can be principally 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, the small grain size promotes the activation of nonbasal dislocation modes enhancing the ductility of the alloys, as seen also in. 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 very abundant small-angle boundaries. As a consequence the dislocation mobility is lowered and the strength is enhanced. The high yield strength in the as-extruded state is attributed mainly to the fine-grained microstructure and the reduced dislocation mobility due to the obstacle action of the IMP particles and the dislocation network. Upon the RHT, slight grain growth and recrystallization 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 the volume fraction and size of the rod- and plate-like IMP particles in the matrix grains, which contributes to the yield stress increase. 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 (MgZn<sub>2</sub>) as reported by Mendis et al. However, for a confident identification of this phase, further studies are necessary. Besides the attractive combination of strength and ductility, another advantage of our alloys is their moderate tension-compression yield stress asymmetry, which is mainly ascribed to the small grain size. It is known for Mg alloys that with decreasing grain size an activation of the twinning deformation mode becomes increasingly difficult. The energy caused by grain boundary incompatibility stresses is assumed to be consumed first by non-basal slip than twin formation. Upon the RHT, the tension-compression yield stress asymmetry decreases in all alloys compared to the as-extruded state. Reduced tension-compression yield stress asymmetry can be attributed to a weakening of the crystallographic texture as well as a decreased dislocation density and the associated reduced stress concentrations at which twinning would preferentially be initiated. The latter effect was observed in this study, while detailed analysis of the crystallographic texture is part of an up-coming work. Weak texture, however, was observed in alloys similar in composition and fabrication as those presented here. Upon aging the tension-compression yield stress asymmetry increases somewhat. On the one hand, they decorate dislocations and impede their motion. [Zhang 2012, Zhang J. 2014, Panda 2016b, Niu 2013, Gibson 2010, Panda 2016a, StJohn 2005, Janz 2009]

#### **2.4 The production process**

Mg alloys can be manufactured by various methods [D.H. StJohn 2005]. The choice of a particular method depends on many factors such as the targeted component properties, shape, dimensions, the ability to cast an alloy and the number of parts to be synthesized [Mordike, B. 2001]. Casting is the predominant process to manufacture magnesium parts and implants. This process starts with the production of metallic ingots from which the implants will be made. Casting is suitable for the production of small series of near net shape components as well as for the mass production with high dimensional precision. Metallic parts can be cast either directly into the shape of the component or as ingots that can be subsequently shaped into a desired form using other forming processes. The growth rate of crystalline phases is much higher in the liquid state than in the solid state, the microstructure of as-cast materials is much coarser than that of heat-treated or

annealed metals. Melting of most implant metals is performed under vacuum condition. The use of vacuum in melting operations is used not only to prevent reactions such as oxidation, but to prevent, and even remove, dissolved gases in the metals in order to avoid porosity. The nature and purity of the elemental material components mixed prior to melting, together with melt practice itself, have an influence on homogeneity, porosity and microcleanliness of the cast alloy. The limitations of casting are dependent on the casting parameters and could appear as segregations, precipitation shrinkage, micro- and macroporosity, inhomogeneous grain size and grain size distribution during solidification. Moreover, the mechanical properties can be tailored by appropriate thermal treatments at different temperatures and for various 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 recrystallization heat treatments, and precipitation hardening.

Casting is generally only used as the primary fabrication process and consequently, other forming and thermo-mechanical processes are performed to achieve the desired shape and mechanical properties. The mechanical working of implant metals can be accomplished by various processes, including forging, rolling, and extrusion which are usually performed at elevated temperatures.

Wrought materials are preheated prior to deformation to dissolve precipitates and to activate additional slide systems in magnesium base materials with a hexagonal close-packed (h.c.p.) crystal structure. Depending on the wrought process and its parameters (i.e. deformation ratio, deformation speed, billet temperature), it is possible to achieve a magnesium alloys with a fine grained, homogeneous microstructure. Such hot working processes break down the cast structure and improve mechanical properties by plastic deformation and work hardening mechanisms. Optimal hot working temperatures are selected in the range that the alloy is easily workable and the surface oxidation in air is not too severe. Following hot working, metals are cold worked and heat-treated to obtain final dimensions with desired physical and mechanical properties. The combination of different processing steps, heat treatments and the variety in the alloy composition influences the microstructure – property relationship and can lead to drastic differences in strength, ductility, creep resistance and corrosion performance. Therefore, the process chain has to be configured according to the intended application and its requirements. Recently, design strategies aiming at substantial grain

Additive manufacturing (AM) or 3D printing of metals has received significant attention as a fabrication technique to produce highly accurate and complex-shaped structures such as patient-specific fixation hardware.

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, with properly and 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).

[Mordike 2001, Peng 2013, Novakova-Marcincinova 2014a, Yang 2011, Zhao 2015, Kuric 2016]

#### **2.5 Degradation properties**

An overview of the results is presented in Fig. 1 as the average corrosion rate  $\pm$  standard error. Each point in the graph



represents the average corrosion rate for one of the materials, calculated from the corrosion rates at different time points and collected from different studies. In addition, different implantation sites and corrosion media were included in that average.

It can be observed from Fig. 1 that the corrosion rate in vivo is described by a smaller range of values than is the in vitro corrosion rate.

### 3 MATERIAL AND METHODS

In this study, the degradable Mg–Al–Zn–Nd–Zr alloy, which has been proven to have proper mechanical properties and enhanced corrosion resistance, is produced and its antibacterial activity is tested. By monitoring the in vitro and in vivo antibacterial activity, degradation property and cytotoxicity, Mg–Al–Nd–Zn–Zr alloy presents enhanced antibacterial properties, biocompatibility, and corrosion resistance.

In the experiments were studied Mg–Al–Zn–Nd–Zr alloy sheet (wt. fraction: Al (0.013 %), Zn (0.24 %), Nd (2.09 %), Zr (0.49 % balance Mg) of thickness 4mm was cut into rectangular samples with dimensions of 30×20 mm<sup>2</sup>. All alloys were cast and then hot deformation, with deformation ratios between 10:1 and 40:1.

The samples after ED are designated as AZ80-MAO-ED. Tension and compression tests were carried out with a MTS 810.22 universal testing machine, according to ASTM E8-04 and ASTM E9-89a (2000) [Gibson 2010, Guan 2014]. The tensile samples had a gauge length of 35 mm and the compressive samples had diameter of 6 mm and a height of 9 mm. A crosshead speed of 0.5 mm min<sup>-1</sup> was used.

The surface morphology and elemental composition of the samples were examined by scanning electron microscopy (SEM; Philips XL30 FEG SEM) coupled with energy-dispersive X-ray spectroscopy (EDS; EDAX Si/Li detector).

[StJohn 2005, Janz 2007, Janz 2009, Yang 2011, Barfield 2012, Hiromoto 2015, Seitz 2014, Zhao 2015, Kuric 2017a]

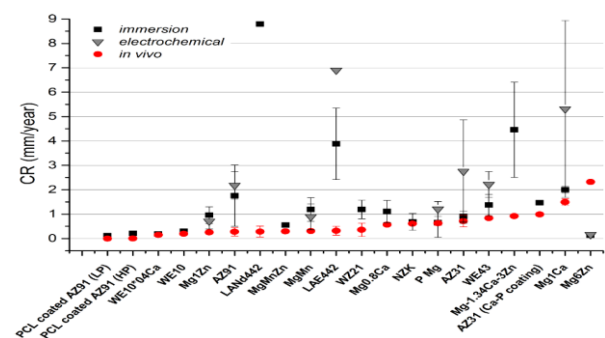


Figure 1. Comparison of the averaged in vitro and in vivo corrosion rates of 20 different materials [StJohn D.H. 2005]

### 4 RESULTS AND DISCUSSION

Fig. 1 shows the micrographs of the surface and the cross section of the samples. A flake-like microstructure on the surface (Fig. 2 b).

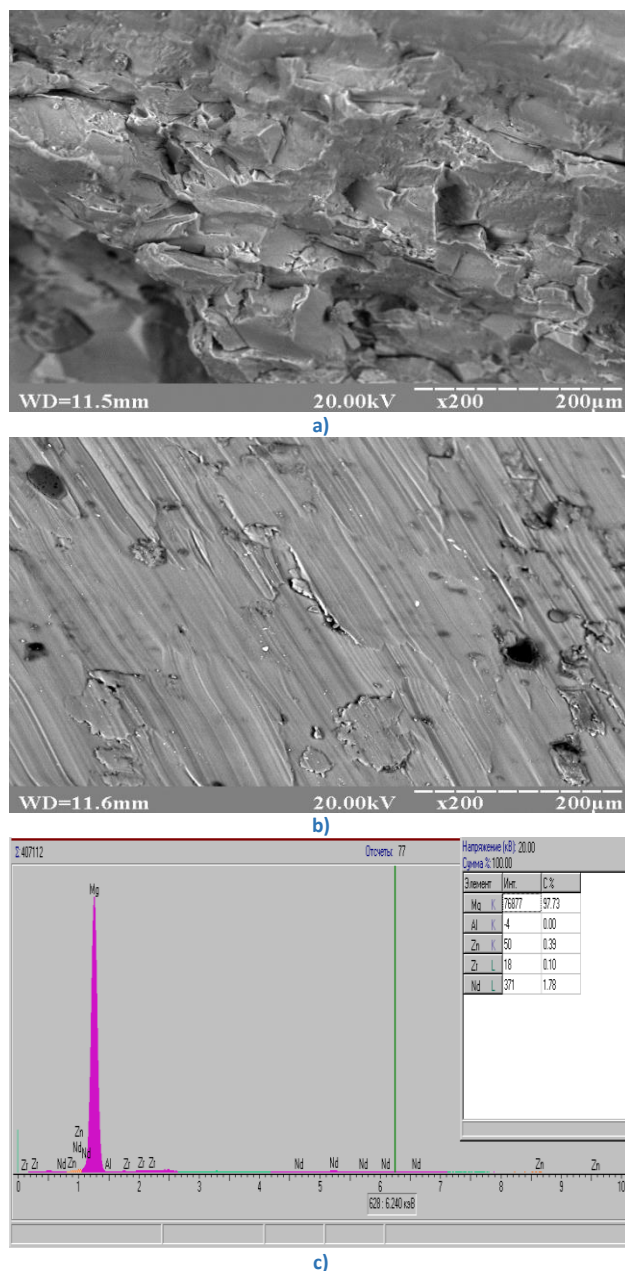


Figure 2. Morphology of (a) surface and (b) cross section of Mg-alloy, (c) EDX analysis.

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

The high yield strength in the as-extruded state is attributed mainly to the fine-grained microstructure and the reduced dislocation mobility due to the obstacle action of the IMP particles and the dislocation network. However, for a confident identification of this phase, further studies are necessary. Besides the attractive combination of strength and ductility, another advantage of our alloys is their moderate tension compression yield stress asymmetry, which is mainly ascribed to the small grain size. It is known for Mg alloys that with decreasing grain size an activation of the twinning deformation mode becomes increasingly difficult. The energy caused by grain boundary incompatibility stresses is assumed to be consumed first by non-basal slip than twin formation. Upon the RHT, the tension-compression yield stress asymmetry

decreases in all alloys compared to the as-extruded state. Reduced tension-compression yield stress asymmetry can be attributed to a weakening of the crystallographic texture as well as a decreased dislocation density and the associated reduced stress concentrations at which twinning would preferentially be initiated. The latter effect was observed in this study, while detailed analysis of the crystallographic texture is part of an up-coming work. Weak texture, however, was observed in alloys similar in composition and fabrication as those presented here. Upon aging the tension-compression yield stress asymmetry increases somewhat.

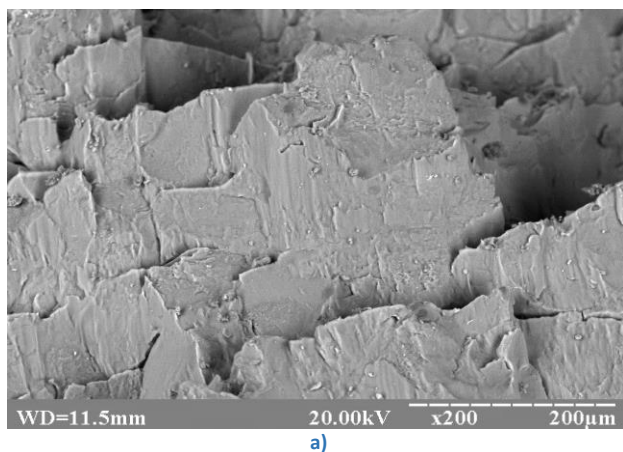
The reason for this behaviour is the different mode of loading in tension and compression. While porosity is affecting tension properties negatively and as well the calculation of the elastic modulus this is not the fact in compression. Under compression all pores will be closed first and will not lead to initial cracks and crack propagation. In fact pores are present in all castings. Due to shrinkage during solidification and that feeding is not possible in all cases under standard solidification conditions microporosity is present.

Fig. 2 shows the micrographs of the surface and the cross section of the samples after deformation (less than 40%).

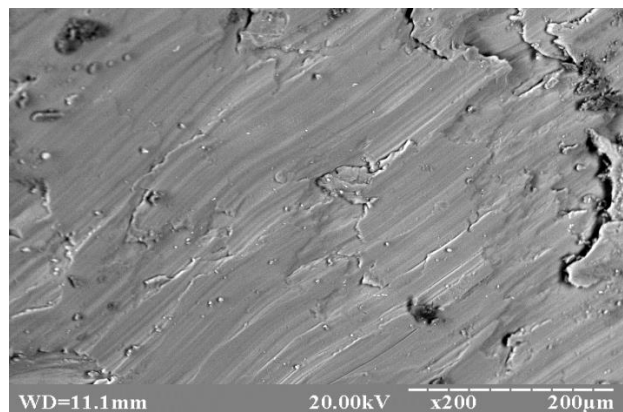
After the thermo-mechanical processing the grain size of the Mg–Al–Zn–Nd–Zr alloys was very small (Fig. 3). We attribute this fact to the fine-grained microstructures of the castings, the appropriately chosen extrusion parameters and the presence of grain-boundary-pinning IMP particles, which hinder grain growth during thermo-mechanical forming.

The energy caused by grain boundary incompatibility stresses is assumed to be consumed first by non-basal slip than twin formation. When considering Nd as alloying element in our design strategy, it was expected that addition of Nd would result in an improvement in the degradation resistance by incorporating neodymium into the Mg matrix and in an increase in strength by the formation of Mg – Nd strengthening phases. Our analyses show that the extend of recrystallization was moderate in as-extruded alloys, but noticeably enhanced in RHT specimens. Complete recrystallization, however, could not be achieved in our experiments.

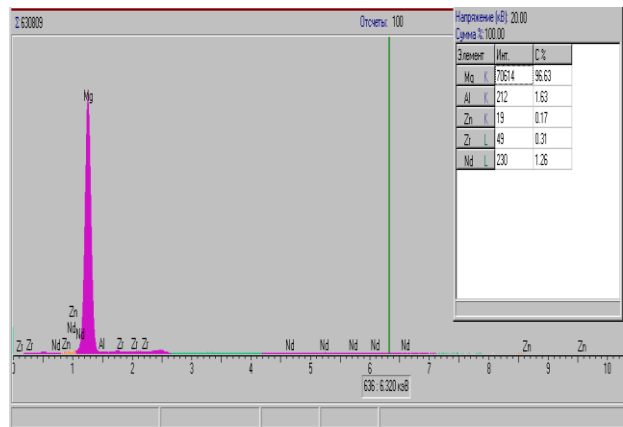
[Zhang J. 2014, Niu 2013, Zhang 2012, Novakova-Marcincinova 2013, Friedrich 2006, Kuric 2017b, ASTM B296-03. 2014, Song 2007, Barfield 2012]



a)

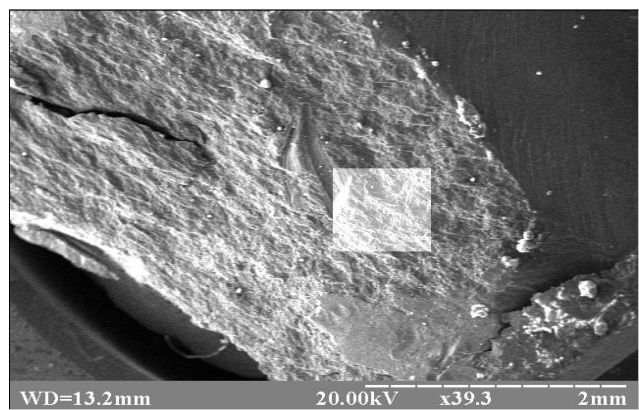


b)

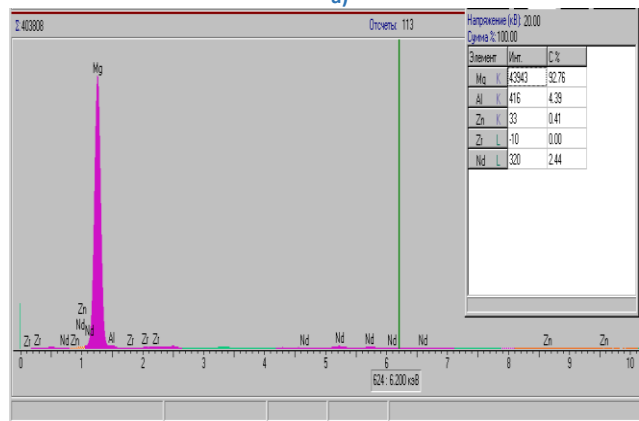


c)

Figure3. Morphology of (a) surface and (b) cross section of Mg-alloy, (c) EDX analysis.



a)



b)

Figure 4. Morphology of (a) surface and (c) EDX analysis (590°C, 2 minute, less than 40%)

## 5 CONCLUSIONS

The implant material has to achieve certain degradation behaviour, strength under tension, compression, bending and torsion as well as fatigue values to assure the proper mechanical behaviour as well as to avoid e.g. stress shielding as much as possible when a material is used as a bone implant. All these factors are basically based on the microstructure. Microstructure formation is due to alloying elements and processing parameters. As a next step it is therefore recommended to select alloying elements in combination with a processing route that produces materials with a property profile that is as close to the bone in the area of application. On the basis of microstructures, mechanical and degradation properties and biocompatibility, the following conclusions can be drawn: the average grain size of Mg–Al–Zn–Nd–Zr alloys was decreased with the increment of Zr concentration owing to the recrystallization process during the deformed process. The mechanical properties of Mg–Al–Zn–Nd–Zr alloys were improved by fine grain size and homogeneous secondary precipitates.

In this study Mg–Al–Zn–Nd–Zr 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, with properly and 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 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 recrystallization heat treatments, and precipitation hardening. The influence of Yb on the alloy performance was studied. The main function of Nd 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 Nd to magnesium alloys significantly improved the alloy's cast ability and slightly improved its mechanical performance. Nd is found in grain-boundary-pinning particles, which hinder grain growth during hot extrusion and during subsequent heat treatments. In summary, the mechanical performance of the alloys is considered promising for temporary implant applications in osteosynthesis.

## ACKNOWLEDGMENTS

The authors would like to thank the KEGA grant agency for supporting research work and co-financing the project KEGA: 004TUKE-4/2017.

## REFERENCES

[ASTM B296-03. 2014] ASTM B296-03(2014), Standard Practice for Temper Designations of Magnesium Alloys, Cast and

Wrought, ASTM International, West Conshohocken, PA, 2014, www.astm.org

[Barfield 2012] Barfield, W., Colbath, G., DesJardins, J.D., Yuehwei, H.A., Hartsock, L. A., The potential of magnesium alloy use in orthopaedic surgery. *Curr Orthop Pract* 2012;23:146–50.

[Berglund 2012] Berglund, I. S. et al., Synthesis and characterization of Mg-Ca-Sr alloys for biodegradable orthopedic implant applications. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, 2012. 100(6): p. 1524-1534.

[Cao 2006] Cao, H., Zhu, J., Zhang, C., Wu, K., Saddock, N. D., Jones, J. W., Pollock, T. M., Schmid-Fetzer, R., Chang, Y. A. Experiments coupled with modeling to establish the Mg-rich phase equilibria of Mg-Al-Ca, *Z. Metallkd.* 97 (2006) 422-428.

[Friedrich 2006] Friedrich, H. E., Mordike, B. L. Magnesium technology. Berlin, Heidelberg: Springer-Verlag; 2006. p. 219.

[Gibson 2010] Gibson, I., Rosen, D. W. and Stucker, B. Additive manufacturing technologies. 2010: Springer.

[Guan 2014] Guan, X., Xiong, M., Zeng, F., Xu, B., Yang, L., Guo, H. et al. Enhancement of osteogenesis and biodegradation control

[Gundea 2011] Gundea, P., Hdnzia, A. C., Sologubenkob, A. S., Uggowitzera, P. J. High-strength magnesium alloys for degradable implant applications *Materials Science and Engineering A* 528 (2011) 1047–1054

[Hiromoto 2015] Hiromoto, S. et al., In vitro and in vivo biocompatibility and corrosion behaviour of a bioabsorbable magnesium alloy coated with octacalcium phosphate and hydroxyapatite. *Acta biomaterialia*, 2015. 11: p. 520-530.

[Janz 2007] Janz, A., Gröbner, J., Mirkovic, D., Zhu, J., Chang, Y. A., Schmid-Fetzer, R. Experimental study and thermodynamic calculation of Al-Mg-Sr phase equilibria, *Intermetallics*, 15(4) (2007) 506-519.

[Janz 2009] Janz, A., Gröbner, J., Cao, H., Zhu, J., Chang, Y.A., Schmid-Fetzer, R. Thermodynamic modeling of the Mg-Al-Ca system. *Acta Mater.* 2009, 57, 682–694.

[Koike 2003a] J. Koike, *Mater. Sci. Forum.* 449–452 (2004) 665–668.

[Koike 2003b] Koike, J., Kobayashi, T., Mukai, T., Watanabe, H., Suzuki, M., Maruyama, K., Higashi, K. *Acta Mater.* 51 (2003) 2055–2065.

[Kuric 2016] Kuric, I., Zajacko, I., Cisar, M. Analytical Intelligence Tools for Multicriterial Diagnostics of CNC Machines. In : *Advances in Science and Technology-Research Journal* Volume: 10 Issue: 32 Pages: 59-64 Published: DEC 2016

[Kuric 2017a] Kuric, I., Dodok, T., Cubonova, N. Workshop Programming as a Part of Technological Preparation of Production In : *Advances In Science And Technology-Research Journal* Volume: 11 Issue: 1 Pages: 111-116 Published: MAR 2017

[Kuric 2017b] Kuric, I., Cisar, M., Cubonova, N. Design of equipment for training machine tools In : *MATEC Web of Conferences* Volume: 94 Article Number: UNSP 01003 Published: 2017

[Lock 2014] Lock, J. Y. et al. Degradation and antibacterial properties of magnesium alloys in artificial urine for potential resorbable ureteral stent applications. *Journal of Biomedical Materials Research Part A*, 2014. 102(3): p. 781-792.

[Luo 2012a] Luo, A. A., Powell, B. R., Sachdev, A. K. Computational phase equilibria and experimental investigation of magnesium-aluminum-calcium alloys. *Intermetallics* 2012, 24, 22–29.

[Luo 2012b] Luo, A. A., Fu, P., Peng, L., Kang, X., Li, Z., Zhu, T. Solidification microstructure and mechanical properties of cast



magnesium-aluminum-tin alloys. *Met. Mater. Trans.* 2012, 43A, 360–368.

[Mordike 2001] Mordike, B. and Ebert, T. Magnesium: Properties—applications—potential. *Materials Science and Engineering: A*, 2001. 302(1): p. 37-45.

[Niu 2013] Niu, J., Yuan, G., Liao, Y., Mao, L., Zhang, J., Wang, Y. et al. Enhanced biocorrosion resistance and biocompatibility of degradable Mg-Nd-Zn-Zr alloy by brushite coating. *Mater Sci Eng C Mater Biol Appl* 2013;33:4833e41.

[Novakova-Marcincinova 2013] Novakova-Marcincinova, L., Novak-Marcincin, J. Selected Testing for Rapid Prototyping Technology Operation In: *Applied Mechanics and Materials*. Vol.308(2013),p.25-31.-ISSN1662-7482

[Novakova-Marcincinova 2014a] Novakova-Marcincinova, L., Novak-Marcincin, J. Production of composite material by FDM rapid prototyping technology In: *Applied Mechanics and Materials : Novel Trends in Production Devices and Systems*. Vol. 474 (2014), p. 186-191. - ISSN 1662-7482

[Novakova-Marcincinova 2014b] Novakova-Marcincinova, L., Novak-Marcincin, J. Production of ABS-Aramid Composite Material by Fused Deposition Modeling Rapid Prototyping System In: *Manufacturing Technology*. Vol. 14, no. 1 (2014), p. 85-91. - ISSN 1213-2489

[Panda 2011] Panda, A. et al. Analytical expression of T-vc dependence in standard ISO 3685 for cutting ceramic. In: *Key Engineering Materials*. 2011, Vol. 480-481 (2011), p. 317-322. ISSN 1013-9826

[Panda 2013] Panda, A. et al. Roller bearings and analytical expression of selected cutting tools durability in machining process of steel 80MoCrV4016. In: *Applied Mechanics and Materials*, ICACME 2013, 2nd International Conference on Automatic Control and Mechatronic Engineering, Bangkok, Thailand, 21-22 June 2013. Vol. 415 (2013), p. 610-613. ISBN 978-303785865-3, ISSN 1660-9336

[Panda 2016a] Panda, A., Jurko, J., Pandova, I. Monitoring and Evaluation of Production Processes. An Analysis of the Automotive Industry. Monograph, Springer International Publishing, Switzerland, 2016, (8.4.2016), 117 pages, ISBN 978-3-319-29441-4

[Panda 2016b] Panda, A., Jurko, J., Valicek, J., Harnicarova, M., Pandova, I. Study on cone roller bearing surface roughness improvement and the effect of surface roughness on tapered roller bearing service life. In: *The International Journal of Advanced Manufacturing Technology*. Springer London Ltd, pp. 1099-1106, Volume 82, Issue 5-8, 2016, ISSN 0268-3768

[Pandova 2014] Pandova, I. Nitrogen oxides reduction by zeolite sorbents in manufacturing use. In: *Advanced Materials Research*. 2014, Vol. 937 (2014), p. 487-490. ISSN 1022-6680

[Pandova 2016] Pandova, I. Manufacturing technologies in automotive production and waste water cleaning on zeolite in view of copper. In: *MM Science Journal*. 2016, Vol. 2016 (2016), p. 1218-1221. ISSN 1803-1269

[Peng 2013] Peng, Q., Li, K., Han, Z., Wang, E., Xu, Z., Liu, R., Tian, Y. Degradable magnesium based implant materials with anti-inflammatory activity, *J. Biomed. Mater. Res. A* 101 (2013) 1898–1906.

[Purnama 2010] Purnama, A., Hermawan, H., Couet, J., Mantovani, D. Assessing the biocompatibility of degradable metallic materials: State-of-the-art and focus on the potential of genetic regulation, *Acta Biomaterialia* 6 (2010) 1800–1807

[Rad 2012] Rad, B. et al. Characterization and corrosion behavior of biodegradable Mg-Ca and Mg-Ca-Zn implant alloys. *Applied Mechanics and Materials*, 2012. 121: p. 568-572.

[Seitz 2014] Seitz, J. M. et al. Magnesium degradation products: Effects on tissue and human metabolism. *Journal of*

*Biomedical Materials Research Part A*, 2014. 102(10): p. 3744-3753.

[Schmid-Fetzer 2012] Schmid-Fetzer, R., Gröbner, J. Thermodynamic Database for Mg Alloys—Progress in Multi component Modeling, *Metals* 2012, 2, 377-398

[Song 2007] Song, G. Control of bio degradation of bio compatible magnesium alloys. *Corr Sci* 2007;49:1696–701.

[StJohn 2005] St.John, D. H., Qian, M., Easton, M. A., Cao, P., Hildebrand, Z. *Metall. Mater. Trans. A* 36 (2005) 1669–1679.

[Sun 2012] Sun, Y. et al. Preparation and characterization of a new biomedical Mg–Zn–Ca alloy. *Materials & Design*, 2012. 34: p. 58-64.

[Wu 2002] Wu, M. H. Fabrication of nitinol materials and components. *Shape Mem. Mater. Appl.-Mater. Sci. Forum* 2002, 394–395, 285–292.

[Yang 2011] Yang, S., Min, Q., Chen, Y., Ping, S. MAO-DCPD composite coating on Mg alloy for degradable implant applications, *Materials Letters* 65 (2011) 2201–2204, doi:10.1016/j.matlet.2011.04.037

[Zaborowski 2007] Zaborowski Ekowytwarzanie. Gorzow, pp. 100

[Zhang 2012] Zhang, X. et al. Biocorrosion properties of as-extruded Mg–Nd–Zn–Zr alloy compared with commercial AZ31 and WE43 alloys. *Materials Letters*, 2012. 66(1): p. 209-211.

[Zhang 2014] Zhang, F., Xu, H. H., Du, Y., Schmid-Fetzer, R., Zhou, T. Phase equilibria of the Mg-La-Nd system at 500 °C, *J. Alloys Compd.* 585 (2014) 384-392.

[Zhang J. 2014] Zhang, J., Kong, N., Niu, J., Shi, Y., Li, H., Zhou, Y. et al. Influence of fluoride treatment on surface properties, biodegradation and cytocompatibility of Mg-Nd-Zn-Zr alloy. *J Mater Sci Mater Med* 2014;25:791e9.

[Zhao 2015] Zhao, J., Chen, L.-J., Yu, K., Chen, Ch., Dai, Y.-I., Qiao, X.-y. Biocompatibility of Mg–6%Zn–10%Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> implant, *Trans. Nonferrous Met. Soc. China* 25(2015) 824–831.

#### CONTACTS:

Prof. Eng. Anton Panda, PhD.

Technical University of Kosice

Faculty of Manufacturing Technologies with a seat in Presov,

Sturova 31, 080 001 Presov, Slovak Republic

e-mail: anton.panda@tuke.sk