Charles University

Faculty of Mathematics and Physics

HABILITATION THESIS

Development of ultrafine-grained biodegradable magnesium alloys with tailored microstructure

RNDr. Peter Minárik, Ph.D.

Prague 2021

Content

Acknowledgements

First of all, I would like to thank all of my colleagues from the Department of Physics of Materials, Charles University, who keep helping me on daily basis, and without them, none of this would be possible. My special thanks go to Doc. Dr. rer. nat. Robert Král, Ph.D. and Prof. RNDr. Miloš Janeček, CSc., for their guidance, motivation, support and inspiring discussions since my bachelor studies.

I wish to express gratitude to all my colleagues from domestic and foreign institutions, who significantly contributed to the research summarized in this thesis. Their hard work and our fruitful discussions were crucial during solving many scientific problems. I would like to mention especially Prof. J. Čížek from the Department of Low Temperature Physics, Charles University; Dr. J. Kubásek and Dr. E. Jablonská from University of Chemistry and Technology, Czechia; Dr. J. Bohlen and Dr. S. Yi from Helmholtz-Zentrum Hereon, Germany; and prof. B. Hadzima form University of Žilina, Slovakia.

Finally, I would like to thank all my relatives for their unconditional support.

Preface

First modern metallic biomaterials were basically inert materials such as stainless steel and titanium. Later, surface treatments were used to enhance the interaction of the implant with the surrounding tissue. Finally, the interest has turned into materials that may degrade while the surrounding tissue recovers. Magnesium is considered as the premium candidate for biodegradable metallic material due to high biocompatibility and the fact that the human body is able to discharge a high amount of magnesium without any adverse effect. Low modulus of elasticity is another key feature of magnesium alloys allowing to design so-called isoelastic implants (i.e. load-bearing implants with elastic modulus similar to that of bone tissue). However, early experiments showed unsatisfactory strength and ductility as well as poor corrosion properties (corrosion rate and uniformity) of magnesium-based materials and the necessity of their further improvement. Many research groups started to work in this scientific field during the last two decades with a focus on evaluating the effect of alloying elements and thermo-mechanical processing on the improvement of strength, the reduction of corrosion rate and the improvement of biological response. The general outcome of this research is that the most promising materials combine the synergic effect of a specific alloy composition and tailored microstructure. In particular, the ultrafine-grained condition was found to be very beneficial for improvement of mechanical and corrosion properties. Understanding the effect of grain refinement down to the sub-micrometer range on mechanical, corrosion and biocompatibility properties became one of the big challenges of research of magnesium alloys.

This habilitation thesis contains 9 scientific papers published in respected journals over the last 8 years. All selected papers contributed to the extension of scientific knowledge in the field of biodegradable implants and texture formation during ECAP. The main goal of this still ongoing research is to develop biodegradable magnesium material, which has appropriately low and well controllable degradation rate, high strength and weak texture. The thesis is divided into two thematic sections reflecting the two classes of Mg alloys. The first chapter summarizes results achieved on the Mg-(Li)-Al-RE alloys, which were the first ones in which the beneficial effect of ultra-fine grained microstructure on both mechanical strength and corrosion properties was established. The second chapter presents the subsequent development of Mg-based aluminum-free biodegradable alloys, in which our interest was more focused on mechanisms of the grain refinement and crystallographic texture formation. The thesis is completed with the original full-length papers, which are thoroughly discussed in the text.

1. Introduction

Magnesium is a biodegradable material with high potential of its applicability in medicine. The current research is focused primarily on the manufacturing of small implants as cardiovascular stents, small screws, wires or pins, and also on larger load-bearing implants designed for orthopedic applications. Magnesium-based materials owing to their good mechanical properties and biodegradability, combine advantages of degradable polymers and non-degradable metals (stainless steel, titanium, Co-Cr alloys, etc.) for temporary applications.

The first trials comprising implantation of small magnesium parts are dated to the late 19th century [1]. However, the poor mechanical strength of the pure metal and fast degradation were strong limiting factors for widespread applicability [2]. Intensive research in the field of biodegradable magnesium alloys burst out twenty years ago [3]. Small implants like stents and small screws were developed fast. They are currently used in clinical trials. Some of them are nowadays already commercially available [4]. Therefore, progress in this scientific field is very fast and reflects the high attention of the scientific community. However, the load-bearing implants for fracture fixation are not available yet and currently, they represent the major research topic. In particular, fixation screws, plates, rods and nails, which are used frequently for fracture fixation, are much larger than stents and have to sustain much higher mechanical stress. Furthermore, due to the much larger surface of the load-bearing implants, it is required that the degradation rate needs to be lower than that of the majority of commercially available Mg-based materials.

The research focused on solving problems related to insufficient strength and corrosion resistance can be divided into two main streams: i) development of new alloys and ii) tailoring the microstructure of the existing alloys. During the last years, commonly used alloying elements were aluminum, zinc, manganese, calcium, zirconium, yttrium and rare earth elements (RE) [5–7]. After two decades of intensive research, the best *in vivo* performance during the long-term implantation was achieved in non-commercial LAE-type (Mg-Li-Al-Mischmetal) alloys [8, 9] and commercial and also non-commercial WE-type (Mg-Y-Mischmetal) alloys [4, 10]. Note that Mischmetal is an alloy of rare earth elements with unspecific composition.

Since the beginning of the modern research of biodegradable magnesium materials, there was an increasing number of reports claiming that there is a strong connection between the corrosion rate and the microstructure. Materials with finer microstructure processed by extrusion [11] and/or ECAP (see below) [12–14], [PM1] showed better corrosion resistance compared to the as-cast counterparts. However, there were also works reporting the deterioration of corrosion resistance by microstructure refinement, or a negligible effect of microstructure on corrosion resistance [15, 16]. It should be noted that corrosion is a complicated process that might be affected by many microstructural features, such as grain size, phase composition, segregation of alloying elements, texture, dislocation density, internal stress etc. Processing of the material affects all of these microstructure factors and, therefore, the final corrosion resistance cannot be simply predicted. Relation of the microstructure to the corrosion properties is an interdisciplinary and complicated problem that is still not fully understood, disregarding the intensive research, which has been performed over the last decades.

The most interesting results, related to both mechanical strength and degradation, were observed in materials processed by severe plastic deformation (SPD) techniques. Processing by SPD usually results in exceptional grain refinement and a significant increase in mechanical strength due to the Hall-Petch relation [17, 18]. Moreover, a positive effect of ultrafine-grained (UFG) structure on the corrosion resistance has been also reported. The most commonly used SPD technique is equal channel angular pressing (ECAP), in which the material is pushed through a die consisting of two intersecting channels of the same cross-section, making an angle of typically 90° [19]. Intensive shear strain corresponding to the equivalent strain of about 115% is imposed on the material after one pass through the die [20]. Since the cross-section of the sample remains unchanged after the pressing, the sample may undergo repetitive passes through the die and very high strains can be attained [21]. ECAP is an attractive process as it can be easily scaled up to prepare relatively large samples [22]. This method is therefore of particular interest, especially for the manufacturing of large load-bearing implants.

The main drawback of all SPD techniques, including ECAP, is that the processing often leads to the formation of a strong texture. The final texture after ECAP significantly depends particularly on the geometry of the die and the rotation of the billet between individual processing steps. This rotation is defined as “route” and there are four types denoted as A, B_A, B_C and C; for detailed information, please see Refs. [23, 24]. As mentioned above, the usual angle between intersecting channels of an ECAP die is 90° and the usual rotation of the billet after each pass is 90° along processing direction – denoted as route B_C. Utilization of the route B_C causes formation of a strong texture in low-alloyed magnesium alloys [25–30], [PM4]. Commonly, the texture strength is more than 15 times random, with only one (0001) fiber component oriented ~45-55° from the processing direction. Because of the predominant activation of the basal slip systems, employing a different route causes the formation of a comparably strong texture, but in a different position with respect to the sample coordinate system [31]. As implants usually need to sustain multiaxial loading, strong texture is obviously highly undesirable. Consequently, the investigation of possibilities of strong texture suppression became a very important topic.

2. Alloys containing aluminum

The beginning of the modern research of the biodegradable magnesium alloys is considered to be the study published in 2003, which reported the degradation of coronary stents manufactured from the AE21 (Mg-2Al-1RE, wt. %) alloy in domestic pigs [3]. Soon later, it was found that the experimental LAE442 (Mg-4Li-4Al-2RE, wt. %) alloy has one of the best *in vivo* performance from the currently investigated alloys. Relatively low and uniform degradation rate and no negative effect on the surrounding tissue and internal organs made this alloy one of the most suitable candidates for orthopedic applications at that time [32–36]. Therefore, our first investigation was focused on three alloys – AE21, LAE442 and AE42. The AE42 (Mg-4Al-2RE, wt. %) alloy was selected for two reasons: i) the alloy has a double concentration of alloying elements than the AE21 alloy and is the Li-free version of the LAE442 alloy and ii) the AE42 alloy is a well-known commercial alloy with a lot of literature data available.

In our research we focused on the possibility to increase the corrosion resistance and the mechanical strength of these alloys by a significant grain refinement achieved by ECAP. In addition, we wanted to understand the correlation between the microstructure changes and the degradation behavior. Very soon, we have shown that the alloy composition is the decisive parameter affecting the degradation rate of the ECAP-processed material. In addition, the detailed microstructural analysis of the ECAP-processed LAE442 opened new questions related to the formation of an uncommon texture and precipitates, which were thoroughly inspected. Our research led to the preparation of the LAE442 alloy in the ultrafine-grained condition, which exhibited excellent *in vitro* degradation properties in biologic media and cytocompatibility, high strength and weak texture. The following papers document our most important results in this area.

2.1. Mg-Al-RE alloys

[PM1] **P. Minárik**, R. Král, M. Janeček: Effect of ECAP processing on corrosion resistance of AE21 and AE42 magnesium alloys, *Applied Surface Science* 281 (2013), 44–48. IF=2.538

This paper was focused on the understanding of the effect of ECAP and composition on the grain refinement and corrosion resistance of the AE21 and AE42 alloys. Both alloys were supplied in the extruded condition with comparable grain size and the type, the size and the distribution of intermetallic particles. The intermetallic particles were identified by transmission electron microscopy (TEM) as $Al_{11}RE_3$. The only difference between the alloys was that the volume-fraction of these particles was higher in the AE42 due to (two times) higher amount of the alloying elements.

The subsequent ECAP processing was performed using the comparable parameters and led to the comparable grain refinement and comparable fragmentation and redistribution of the intermetallic particles in both alloys. A stripe-like formation of the $Al_{11}RE_3$ particles was disrupted by shear deformation during ECAP and a more uniform distribution was observed in both alloys after the processing. However, the corrosion resistance measurement performed by the electrochemical impedance spectroscopy (EIS) showed that despite the comparable corrosion resistance of both alloys in the extruded condition, a significant increase in the corrosion resistance was observed in the AE42 alloy after ECAP, whereas in the AE21 alloy a significant decline of corrosion resistance occurred. Note that a decrease in the corrosion resistance in both alloys was expected because smaller grain size usually led to increased electrochemical activity at the grain boundary regions. A thorough investigation of the corrosion layer, which formed after 7 days of immersion of the AE42 alloy, revealed that aluminum present in the $Al_{11}RE_3$ particles reacts during the corrosion process and aluminum oxide integrates itself into a porous corrosion layer formed by magnesium hydroxide. Consequently, the layer became more compact and more resistive to electron and mass transfer, suppressing the corrosion kinetics. This result revealed that the amount and distribution of the $Al_{11}RE_3$ particles in the material causes the observed differences in the corrosion resistance. The effect of the $Al_{11}RE_3$ particles was similarly limited in the extruded condition of both alloys because of their stripe-like distribution, which correlates with the comparable corrosion resistance of both extruded alloys. The spatial distribution of these Al-rich particles was improved by the ECAP processing and in the AE42 alloy, their positive effect on the corrosion resistance overwhelmed the negative effect of the smaller grain size. Consequently, the ECAP-processed AE42 alloy exhibited higher corrosion resistance than its extruded counterpart. On the other hand, more rapid corrosion in the ECAP-processed AE21 compared to the extruded condition was mainly controlled by the smaller grain size. The amount of Al-rich particles was too low in the AE21 alloy to improve the protective ability of the corrosion layer.

The main results of this study were: a) shear deformation during ECAP fragments larger intermetallic particles and makes their distribution more uniform and b) ultrafine-grained condition of the material can be beneficial if the formed surface layer is compact and protective enough.

2.2. Mg-Li-Al-RE alloy

[PM2] **P. Minárik**, R.Král, J. Pešička, S. Daniš, M. Janeček: Microstructure characterization of LAE442 magnesium alloy processed by extrusion and ECAP, *Materials Characterization* 112 (2016), 1–10. IF=2.714

Our subsequent research was focused on the LAE442 alloy, which, as mentioned above, was a very promising candidate for biodegradable applications [32–36]. The LAE442 alloy was processed similarly as both aforementioned AE alloys – by extrusion followed by ECAP and resulted in the average grain size of ~1.5 μm. The dominant intermetallic particles were $Al_{11}RE_3$, but small addition of calcium, which was added to improve the biocompatibility, resulted in the formation of the additional Mg_2Ca phase. Microstructural investigation revealed that both processing steps, extrusion and ECAP, caused significant grain refinement and the redistribution of secondary phases similar to results described in Ref. [PM1]. In addition, TEM investigation revealed the formation of nanocrystalline aluminum-rich particles, which were present in the material already after the first pass through ECAP. The particles origin was not determined in this study and according to the selected area diffraction pattern, it was proposed that they are of Al_3Li phase. However, our further work revealed that they are pure aluminum [PM3]. Detail XRD analysis indicated that dissolution of lithium in the magnesium matrix had a significant impact on the magnesium lattice parameters. The *c/a* ratio decreased from 1.624 to 1.610, which correspond to pure magnesium and the investigated alloy, respectively. Texture analysis performed on the inverse pole figures showed that the texture of the ECAP-processed sample was almost the same as in the extruded sample. This contradicted to findings in other similarly processed AE-alloys and available literature data [27–29]. We have explained this difference by the facilitation of non-basal slip systems due to the change in the *c/a* parameter resulting in the different texture formation. This concept was further elaborated in the subsequent research summarized in [PM4].

The main result of this study was a thorough microstructural characterization of the LAE442 alloy in the cast, extruded and ECAP-processed condition, revealing that the final microstructure is similar to that observed in both AE alloys. Therefore, a similar effect of ECAP on the corrosion resistance, as observed in the AE42 alloy, was expected. Moreover, it was shown that the distribution of aluminum after ECAP is controlled by new nanocrystalline particles. Finally, it was shown that lithium caused a significant change in the *c/a* ratio resulting in unexpected texture formation in ECAP-processed LAE442 alloy.

[PM3] **P. Minárik**, J. Čížek, J. Veselý, P. Hruška, B. Hadzima, R. Král: Nanocrystalline aluminium particles inside Mg-4Li-4Al-2RE magnesium alloy after severe plastic deformation, *Materials Characterization* 127 (2017), 248–52. IF=2.892

TEM with much higher resolution revealed that the nanocrystalline particles reported in Ref. [PM2], which form in the LAE442 alloy after the ECAP, are pure aluminum. The particles phase and structure were unambiguously identified by selected area diffraction (SAED) pattern acquired from the individual crystallites, energy-dispersive X-ray spectroscopy (EDS) mapping with enhanced resolution and utilization of automated crystal orientation mapping in TEM (ACOM-TEM). The particles of the size of ~200 nm and the interparticle distance of ~2 μm were randomly distributed in the material processed by eight passes through ECAP. The ACOM-TEM analysis revealed that the average crystalline size in the particles is ~15 nm and their orientation is random with respect to the surrounding magnesium matrix. Positron annihilation spectroscopy (PAS), in particular coincidence Doppler broadening (CDB) technique, revealed that enhanced segregation of aluminum at dislocations occurred during the ECAP. However, the subsequent exposure to elevated temperatures resulted in the fast dissolution of aluminum back into the magnesium matrix. Similar results were obtained by in-situ heating in TEM. Exposure to the temperature 10 °C below the ECAP processing temperature for only 90 s resulted in the formation of a thick $Al_{12}Mg_{17}$ phase shell around the aluminum nanoparticles. Note that $Al_{12}Mg_{17}$ phase is thermodynamically stable in the temperature range of 100-250 °C when the local concentration of Al exceeds ~1-4.5 wt%, [37]. Therefore, the formation of metastable pure aluminum particles was not expected to form in the magnesium alloy with such a low concentration of aluminum and their origin was not completely understood until now. Nevertheless, it is assumed that the synergic effect of a decrease in the *c/a* ratio due to dissolved lithium and high hydrostatic pressure together with high plastic deformation during ECAP cause the formation of these particles. Note that in similarly processed lithium-free AE42 alloy the formation of Al nanoparticles nor the segregation of Al into dislocations were observed.

In this study, we proved that in LAE442 alloy, enhanced segregation of Al into open volumes, including dislocations, resulted in the formation of metastable aluminum nanoparticles in the magnesium matrix.

2.3. Mg-(Li)-Al-RE alloys – strength and texture formation

[PM4] **P. Minárik**, R. Král, J. Čížek, F. Chmelík: Effect of different c/a ratio on the microstructure and mechanical properties in magnesium alloys processed by ECAP, *Acta Materialia* 107 (2016): 83–95. IF=5.301

Significant differences of mechanical properties of the ECAP-processed AE-alloys (AE21, AE42) and LAE442 alloy were observed. Uniaxial tensile/compression testing along the processing direction showed that both AE alloys exhibit a typical decrease in the yield strength (both compression and tensile) with an increasing number of ECAP passes. Such a decrease is caused the formation and intensification of the (0001) texture component oriented ~50° from the processing direction. As mentioned in the Introduction, the formation of this component is common in magnesium alloys processed by ECAP via route B_C and originates from predominant activation of the basal slip system. The high strength of this component causes the texture softening during the deformation along the processing direction, which can overwhelm the grain boundary strengthening resulting from the significant grain refinement achieved by ECAP. This scenario holds for the microstructure, texture and mechanical properties evolution in both AE alloys. On the contrary, the yield strength of the LAE442 gradually increased with an increasing number of ECAP passes. The different texture formation in LAE442 causes this discrepancy. A thorough texture analysis revealed that there are two additional texture components in the ECAP-processed LAE442 alloy which cause a significant decrease in the overall strength of the undesired basal slip component. The formation of these new components in the ECAP-processed LAE442 alloy was identified for the first time in this paper. It was explained by the massive activation of <a> prismatic and <c+a> second order pyramidal slip system during ECAP. Increased activity of non-basal slip systems was attributed to the lithium addition in the LAE442 alloy, which caused a significant decrease in the *c/a* ratio.

PAS analysis revealed that enhanced activity of the non-basal slip systems did not only cause a change in the texture formation but it caused also a change in the evolution of dislocation density with an increasing number of ECAP passes. This evolution, namely the significant increase in the dislocation density after the first pass through ECAP and subsequent gradual decrease, was qualitatively similar to that in both AE- and other low-alloyed magnesium alloys processed similarly. However, quantitatively, the increase in dislocation density in LAE442 was more than by one order of magnitude higher than in AE alloys, exceeding 2.10^{14} m^{-2}.

The effect of both texture and dislocation density on the evolution of the mechanical strength after ECAP was explained by the microhardness measurement. Unlike the evolution of the yield strength, the microhardness of all three alloys gradually increased with an increasing number of ECAP passes. Vickers microhardness introduces a multiaxial loading to the material and the texture effects are significantly suppressed. Comparison of microhardness evolution with the grain size evolution in terms of the Hall-Petch (H-P) relation [17, 18] revealed that both AE alloys follow the H-P relation well, have comparable H-P parameters and differ only in a constant representing the higher strength in the higher alloyed alloy - AE42. Therefore, it was concluded that grain boundary strengthening is the dominant factor affecting the strength of both AE-alloys. On the other hand, the data measured for the LAE442 alloy did not follow the H-P relation at all. However, after taking into account the dislocation strengthening and the Taylor factor [38], the corrected data followed the H-P relation well. Consequently, the higher dislocation density in the LAE442 alloy caused that the material strength depended on both grain size and the dislocation density.

The main results of this study were: a) the formation of so far unknown texture components resulting from the enhanced activity of the non-basal slip system was presented and fully explained and b) the correlation between the individual strengthening mechanisms and the material strength was found for all three investigated alloys. This study showed that the texture development in magnesium alloys processed by ECAP can be effectively tailored by modification of the *c/a* ratio, and, consequently, the negative effect of texture on the mechanical strength can be avoided.

2.4. *In vitro* degradation of Mg-Li-Al-RE alloy

[PM5] **P. Minárik**, E. Jablonská, R. Král, J. Lipov, T. Ruml, C. Blawert, B. Hadzima, F. Chmelík: Effect of equal channel angular pressing on in vitro degradation of LAE442 magnesium alloy, *Materials Science and Engineering: C* 73 (2017), 736–42. IF=5.080

Concurrently with our previous investigation [P1-P3], additional *in vivo* studies reported excellent biodegradable properties of the LAE442 alloy in the extruded condition, including the long-term 3.5-year degradation period [8, 9, 11, 32–36]. Therefore, the major question was whether our ECAP-processed LAE442 alloy can exhibit even better performance than its extruded counterpart and this way the application potential of the LAE442 alloy in medicine could be extended increase. Consequently, the main focus of this study was to explore the effect of ECAP on the degradation rate of this alloy and whether the processing does not compromise the biocompatibility of the alloy. At first, a thorough investigation of the corrosion properties in 0.1 M NaCl solution was performed by electrochemical corrosion tests and hydrogen evolution test. The results of EIS showed that the ECAP processed sample has superior corrosion resistance in comparison with the extruded state. In addition, the hydrogen evolution test showed that the degradation rate becomes linear in time within two days of immersion and the ECAP processed material degrades with a significantly slower rate, compare 2.87(3) and 2.49(2) mg/cm^2/day for the extruded and ECAPed samples, respectively. The increase in the corrosion resistance was attributed to the similar effects as discussed in Ref. [PM1]. In addition, the positive effect of Li(OH) on the surface layer was proposed, but this assumption was not experimentally proved.

Subsequent investigation of the degradation properties was performed in two biological media. Kirkland's biocorrosion medium (KBM) was chosen as a simulated body fluid (SBF) because, as mentioned in [3], it closely reflects the ionic composition of the human plasma, especially with respect to the concentration of Cl^- (contrary to other SBFs). Minimal essential medium (MEM) + 10% FBS was chosen as a cultivation medium and was also used for *in vitro* cytotoxicity testing of the investigated samples. In order to explore the influence of Fetal bovine serum (FBS), KBM + 10% FBS and MEM without FBS were also used in this study. The corrosion rate was calculated from the results of the mass-loss tests after 14 days of immersion. The results showed that the ECAP processed material exhibits a significant decrease of the corrosion rate by ~30%, compared to the extruded condition, in all used biological media. In addition, the degradation was uniform and the measurement of cytotoxicity revealed that the LAE442 alloy has sufficient cytocompatibility disregarding processing (extrusion, ECAP). It is consistent with previously published observations.

The most important result of this study was that the ECAP processing could be used to increase the corrosion resistance of the LAE442 magnesium alloy as a material for temporary orthopedic implants without any adverse effect on biocompatibility. Note that until then, the best corrosion resistance was reported for the extruded condition. This study showed unambiguously that a decrease in degradation rate by an additional 30% might be potentially achieved by ECAP. The results of the degradation rate, cytotoxicity and mechanical strength unambiguously showed that the ECAP-processed LAE442 alloy was a suitable candidate for the subsequent *in vivo* testing.

3. Magnesium-based aluminum-free alloys

The results obtained in the LAE442 alloy were very promising and the subsequent *in vivo* testing was planned. However, in the meantime, the opinion that aluminum shall not be used in the biodegradable magnesium alloys became too strong within the scientific community. The major concern with aluminum was that its dissolution in the human body would lead to long-term complications, especially to the development of Alzheimer disease. Even though no clear proof of such a connection was given the opinion to abandon the Al-containing alloys persisted [39, 40]. In addition, this opinion was supported by successful studies of Mg-Y-RE-Zr alloys, usually represented by the commercial WE43 (Mg-4wt%Y-3wt%RE-0.4wt%Zr) alloy [32, 41–46].

In this regard, our focus moved to exploring possibilities to enhance the important physical properties of the WE43 alloy and to develop a new Al-free alloy with properties superior to the WE43 alloy. Very soon, it was found that the WE43 alloy can also benefit from the UFG microstructure. In addition, it was claimed that the microstructural changes resulting from the ECAP processing of the WE43 alloy are of high scientific interest and deeper insight can increase possibilities for utilization of this alloy in medicine. Therefore, a lot of efforts we have made in this regard, especially with the focus on grain refinement, superplasticity and texture formation. Our development of new Al-free alloys for biodegradable applications continues concurrently with this research. However, these results are subject of ongoing research and only some of them are included in this thesis.

3.1. Ultrafine-grained Mg-Y-RE alloy

[PM6] **P. Minárik**, J. Veselý, R. Král, J. Bohlen, J. Kubásek, M. Janeček, J. Stráská: Exceptional mechanical properties of ultra-fine grain Mg-4Y-3RE alloy processed by ECAP, *Materials Science and Engineering: A* 708 (2017), 193–98. IF=3.414

The motivation of investigation of the WE43 alloy was twofold. Firstly, to compare the effect of ECAP on the degradation rate with the previously observed LAE442 alloy [PM5]. Secondly, to investigate the mechanisms of the microstructure refinement during the ECAP processing in this alloy. During ECAP processing of low-alloyed magnesium alloys, mainly the AE-, AZ-, AX-type alloys, it was observed that the grain refinement is more intensive in the areas with a higher concentration of the intermetallic particles. This observation was not surprising because fine particles present in the matrix can effectively pin grain boundaries and suppress the grain growth. In addition, stress concentration in their vicinity during the processing can contribute to the recrystallization processes and increase their rate. Therefore, the major issue was how to take advantage of this finding in further work. The WE43 alloy is a precipitation-hardenable alloy and its precipitates have relatively high thermal stability. The idea was that dynamic precipitation during ECAP will result in the formation of uniform distribution of fine and thermally stable particles with the desired effect on the grain refinement.

The results obtained on the ECAP-processed WE43 alloy even exceeded our expectations. The processing caused the formation of the ultrafine-grain material with an average grain size of only ~340 nm. Note, that the majority of ECAP-processed magnesium alloys exhibit average the grain size in the range of 1-1.5 μm [25, 27, 29, 30, 47–51]. TEM analysis revealed that the oval Mg_5RE intermetallic particles, having an average diameter of ~150 nm, were uniformly distributed in the magnesium matrix, especially at triple junctions. In addition, the texture formed during ECAP processing was weak and comprised only elements corresponding to the activity of the non-basal slip system, as described in Ref. [PM4]. It was found for the first time that the texture element corresponding to the activation of the basal slip system was completely missing in the magnesium alloy processed by ECAP. The investigated material was solution treated prior to the ECAP and the formation of fine distribution of the Mg_5RE particles having an oval character was ascribed to the dynamic precipitation and dissolution of the precipitates during ECAP. Their contribution to grain refinement and texture suppression was discussed. This analysis has been significantly extended in our following work [PM9].

An increase in the mechanical strength caused by the microstructure modification was exceptional. The compression yield strength increased from 125 MPa to 427 MPa, while the plastic deformation to fracture decreased from ~26% down to ~10%. Only several magnesium-based materials exhibited a yield point above 400 MPa. This exceptionally high yield strength has been so far reported only in magnesium-based metallic glasses [52], composites [53] and alloys containing high volume fraction of long-period stacking-ordered (LPSO) phases [54]. The significant increase in compression yield strength was predominantly related to the extraordinary grain refinement and uniform and dense distribution of small Mg_5RE intermetallic particles. In addition, the material also benefited from a weak texture and the absence of the basal slip texture component. Moreover, the ECAP-processed sample exhibited a sharp yield point, which is quite uncommon in magnesium alloys. The proper explanation of this effect was done in our subsequent research performed on the ZN31 alloy, in which the sharp yield point was observed in the ECAP-processed condition as well, see Ref.

[55]. It was shown that the sudden decrease in the strength was caused by extensive twinning, which resulted from a convenient texture, irrespective of its low intensity and the ultrafine-grained condition of the material.

The main result of this study with respect to the biodegradable applications was the exceptional increase of the WE43 alloy strength together with a weak texture. Achieving a very high mechanical strength in this alloy may not look important for biodegradable purposes, but the contrary is true. The higher mechanical strength enables to reduce the volume of the potential implant. The other important outcome of this study was that it was proved that processing of the precipitation-hardenable alloys might benefit from dynamic precipitation acting during the processing.

3.2. Superplastic behavior of Mg-Y-RE alloy

[PM7] **P. Minárik**, J. Veselý, J. Čížek, M. Zemková, T. Vlasák, T. Krajňák, J. Kubásek, R. Král, D. Hofman, J. Strásḱá: Effect of secondary phase particles on thermal stability of ultra-fine grained Mg-4Y-3RE alloy prepared by equal channel angular pressing, *Materials Characterization* 140 (2018), 207–16. IF=3.220

The thermal stability of the ultrafine-grained microstructure is not very important for biodegradable purposes because the application temperature range is low (~37 °C), but achieving the ultrafine-grained structure in the WE43 alloy raised questions related to potential superplastic behavior. Superplasticity is extremely useful for the manufacturing of parts and components having complex shapes, which is exactly the case of medical implants. The thermal stability of the ultrafine-grain microstructure was determined by microhardness, in the temperature range of 160-500 °C. It was shown that the ultrafine-grain microstructure of the ECAP-processed WE43 alloy is stable up to 280 °C for 1 h and only a small decrease in the microhardness was observed after 16 h of annealing at 250 °C. The detail microstructural characterization revealed that the onset of the grain growth correlates with the thermal stability of the Mg_5RE intermetallic particles and the grain growth itself is highly affected by the redistribution (dissolution and growth) of the intermetallic particles in the matrix. Surprisingly, a statistically significant increase in the microhardness was observed in the temperature range of 220-280 °C. The processescontrolling the enhanced temperature stability have been thoroughly investigated by PAS and TEM, including analysis of the coincidence doppler broadening and *in-situ* annealing in TEM. Both *in-situ* and *ex-situ* measurements revealed that solute atoms of Y and RE tend to segregate at the grain boundaries and eventually form Mg-Y-RE intermetallic particles.

The main result of this study was that the ultrafine-grained structure of the WE43 alloy has relatively high thermal stability which is governed by the Mg_5RE intermetallic particles. This finding was of high interest from the l application in biomedicine point of view because potential superplastic behavior may significantly facilitate the manufacturing of implants with complex shapes. In general, this finding was also very important for other potential high-temperature applications of ultrafine-grained Mg-RE alloys.

[PM8] T. Vávra, **P. Minárik**, J. Veselý, R. Král: Excellent Superplastic Properties Achieved in Mg–4Y–3RE Alloy in High Strain Rate Regime, *Materials Science and Engineering: A* 784 (2020), 139314. IF=5.234

This study was focused on the investigation of the potential superplastic behavior of the ECAP-processed WE43 alloy. This study was primarily motivated by the promising results of the thermal stability reported in Ref. [PM7]. The first investigation in this regard revealed that the strain rate sensitivity parameter (m-parameter) is high (~0.6) in the strain rate range of $10^{-1} – 10^{-2}$ s^{-1} at the temperature of 400 °C. Note that an m-parameter exceeding 0.5 is considered to be one of the important indicators of superplasticity [56]. The high m-parameter achieved for rather high strain rates indicated that the material might even exhibit high strain rate superplasticity (HSRS). HSRS is rare in magnesium alloys but extremely useful because the deformation is fast and the material can be easily processed at the industrial-scale level. This indication was also supported by the calculation of the activation energy distribution in the strain rate range of $10^{-3} – 10^{-1}$ s^{-1}, which indicated that the grain boundary sliding should be more active at the strain rate of 10^{-1} s^{-1} than at the lower ones. The subsequent deformation to fracture tests finally confirmed that the investigated material exhibits excellent HSRS. The extremely high ductility of ~1230% was achieved at the strain rate of 10^{-2} s^{-1} and two deformation temperatures: 350 °C and 400 °C. Moreover, the ductility of ~1000% and ~800% was achieved at the strain rate of 10^{-1} s^{-1} and the temperature of 400 °C and 350 °C, respectively. The ductility at the strain rate of 10^{-1} s^{-1} was superior to almost all previously reported materials. The only Mg alloy with higher ductility was Mg-Gd-Y-Zn-Zr alloy prepared by friction stir processing (FSP). It is in fact the record value of elongation within the HSRS regime [57] in Mg-based alloys. However, FSP, unlike ECAP, cannot lead to the preparation of bulk material with a homogenous microstructure; therefore, commercial utilization of superplastic deformation of such material is highly questionable. The final microstructure characterization of the deformed samples revealed that the microstructure remained fine-grained despite the deformation and exposure to the high temperature and cavitation did not occur at the abovementioned deformation conditions.

The main result of this study was the achievement of superplastic behavior of the ultrafine-grained WE43. Moreover, the material exhibited the high strain rate superplasticity with exceptional elongation at the strain rate of 10^{-1} s^{-1}. Therefore, superplasticitic forming may be utilized in the production of pieces made from ECAP-processed WE43 alloy in different areas (biomedicine, transport industry, electronic industry, etc.)

3.3. Mg-Y-RE alloy – processes controlling the refinement and texture formation

[PM9] **P. Minárik**, M. Zemková, J. Veselý, J. Bohlen, M. Knapek, R. Král: The Effect of Zr on Dynamic Recrystallization during ECAP Processing of Mg-Y-RE Alloys, *Materials Characterization* 174 (2021), 111033. IF=4.342(2020)

In this work, the effect of Zr on the Mg_5RE intermetallic particle formation and their contribution to the grain refinement and texture suppression of ECAP-processed WE43 was thoroughly investigated. As mentioned above, the exceptional grain refinement down to ~340 nm and weak texture with components corresponding only to the activation of the non-basal slip systems was observed [PM6]. Dense distribution of small (~120 nm in diameter) Mg_5RE particles effectively suppressed the grain growth during the processing, but their presence significantly contributed to the recrystallization as well. TEM analysis revealed that the presence of these particles increases the stress concentration at grain boundaries and, consequently, facilitates the nucleation of new grains. Our investigation on similarly processed Zr-free version of the WE43 alloy revealed that zirconium interferes with the Mg_5RE particles. The small addition of zirconium facilitates their formation and, consequently, directly reduces the final grain size. Zirconium is usually added to the melt of the WE43 alloy to promote the nucleation rate during casting. However, its positive effect on the Mg_5RE particle formation was unknown before this study.

Similarly, as in LAE442 alloy, the significant contribution of the non-basal texture components to the overall texture of the ECAP-processed WE43 alloy can be associated with a massive activation of <a> prismatic and <c+a> second order pyramidal slip system [PM4]. However, the principal question was why the formation of the texture element corresponding to the activation of the basal slip system was totally suppressed. In general, a texture component is formed during the processing by the activation of a high number of dislocations belonging to a single slip system, which, consequently, rotate the lattice of a grain. Note that the <c+a> second order pyramidal slip system contains six slip planes and the number of dislocations needed for rotation of randomly oriented grain into a preferred orientation by predominant activation of one of the <c+a> slip systems is significantly lower than for the basal slip having only a single slip plane. In addition, the grains which correspond to the <c+a> slip texture component are oriented almost ideally for the formation of the prismatic slip component during the successive processing steps of ECAP when the route B_C is used. Consequently, the high nucleation rate caused that the grains which would form basal slip texture component are more likely to be fragmented and reoriented by the non-basal slip systems. This conclusion was also supported by results obtained on the Zr-free alloy, in which a lower nucleation rate, local texture analysis of deformed grains and intergranular misorientation analysis (IGMA) focused on the intergranular strain and low angle grain boundaries were observed.

The main result of this work was understanding the processes controlling the exceptional grain refinement and the texture formation in Mg-Y-RE magnesium alloys processed by ECAP and the significant role of Zr in these processes. These findings are also directly transferable to other similarly processed precipitation hardenable alloys.

4. Conclusions and future perspectives

Scientific papers presented in this habilitation thesis significantly contributed not only to the development of magnesium-based materials for biodegradable applications but also to the understanding of underlying processes acting during ECAP processing of the magnesium alloys. The most important results achieved in the presented papers are:

- The effects causing different evolution of the corrosion resistance of the ECAP-processed magnesium alloys were analyzed. It was revealed that the negative effect of the finer grain size on the corrosion resistance could be overwhelmed by the formation of a more stable and protective corrosion layer. The distribution of Al-rich particles is very important in this regard.
- The LAE442 alloy was prepared in the ultrafine-grained condition, in which the alloy exhibited the high strength, weak texture, superior corrosion resistance and high biocompatibility. This material is therefore a good candidate for the subsequent *in vivo* investigation.
- The formation of nanocrystalline aluminum particles was revealed in the ECAP-processed LAE442 alloy. The origin of their formation was proposed upon thorough analysis employing advanced electron microscopy methods and positron annihilation spectroscopy.
- The formation of previously unreported texture in ECAP-processed magnesium alloy was found in the LAE442 alloy. The origin of the new texture elements was related to the massive activation of the non-basal slip systems in this alloy. It was proposed that intentional variation of the *c/a* ration can be used to suppress the undesired strong texture, which usually forms in ECAP-processed magnesium alloys.
- Exceptional grain refinement was achieved in the WE43 magnesium alloy processed by ECAP. Dynamic precipitation/dissolution during ECAP resulted in the formation of a high density of small intermetallic particles. In addition, weak texture without the basal slip texture component was found in the processed material. Consequently, the ECAP-processed WE43 exhibited exceptional mechanical strength.
- The processes causing the excellent grain refinement and texture suppression, which act during the ECAP processing of the WE43 alloy, were revealed. The

significant effect of zirconium on the precipitation and, consequently, recrystallization was found.

- High thermal stability of the ultrafine-grained WE43 alloy enabled the activation of the high strain rate superplasticity of the material. Elongations exceeding 1200% and 1000% were measured at the strain rate of 10^{-2} and 10^{-1} s^{-1}, respectively.

Parts of the results of this still ongoing research were also published in other papers and presented in numerous international conferences. Participation of students in this research project led to defending several bachelor and diploma theses. Finally, work on this topic significantly extended our cooperation with several domestic and foreign institutions.

The development of magnesium-based aluminum-free biodegradable magnesium alloys is still one of our primary topics. Investigation of *in vitro* and *in vivo* degradation of the ECAP-processed Mg-Y and Mg-Y-Li alloys is currently our major interest within the ongoing study supported by Ministry of Health of the Czech Republic: *Biodegradable magnesium-based implants with tailored microstructure and defined degradation rate*. The preliminary results are very promising; however, they cannot be included in this thesis because the research is unfinished. In addition, there is a parallel investigation focused on the preparation of (ultra)fine-grained magnesium alloys for biodegradable applications via powder metallurgy. However, this research is still far from the *in vivo* studies, which are currently undertaken on the ECAP-processed material.

5. References

[1] E.C. HUSE. A new ligature? *The Chicago Medical Journal and Exam*. 1878, vol. 1878, no. 172, pp. 2–3.

[2] WITTE, F. The history of biodegradable magnesium implants: A review. *Acta Biomaterialia*. 2010, vol. 6, no. 5, The THERMEC'2009 Biodegradable Metals, pp. 1680–1692. 10.1016/j.actbio.2010.02.028

[3] HEUBLEIN, B., R. ROHDE, V. KAESE, M. NIEMEYER, W. HARTUNG and A. HAVERICH. Biocorrosion of magnesium alloys: a new principle in cardiovascular implant technology? *Heart*. 2003, vol. 89, no. 6, pp. 651–656. 10.1136/heart.89.6.651

[4] WINDHAGEN, H., K. RADTKE, A. WEIZBAUER, J. DIEKMANN, Y. NOLL, U. KREIMEYER, R. SCHAVAN, C. STUKENBORG-COLSMAN and H. WAIZY. Biodegradable magnesium-based screw clinically equivalent to titanium screw in hallux valgus surgery: short term results of the first prospective, randomized, controlled clinical pilot study. *Biomedical Engineering Online*. 2013, vol. 12, p. 62. 10.1186/1475-925X-12-62

[5] AGARWAL, S., J. CURTIN, B. DUFFY and S. JAISWAL. Biodegradable magnesium alloys for orthopaedic applications: A review on corrosion, biocompatibility and surface modifications. *Materials Science and Engineering: C*. 2016, vol. 68, pp. 948–963. 10.1016/j.msec.2016.06.020

[6] RADHA, R. and D. SREEKANTH. Insight of magnesium alloys and composites for orthopedic implant applications – a review. *Journal of Magnesium and Alloys*. 2017, vol. 5, no. 3, pp. 286–312. 10.1016/j.jma.2017.08.003

[7] SEZER, N., Z. EVIS, S.M. KAYHAN, A. TAHMASEBIFAR and M. KOÇ. Review of magnesium-based biomaterials and their applications. *Journal of Magnesium and Alloys*. 2018, vol. 6, no. 1, pp. 23–43. 10.1016/j.jma.2018.02.003

[8] ANGRISANI, N., J. REIFENRATH, F. ZIMMERMANN, R. EIFLER, A. MEYER-LINDENBERG, K. VANO-HERRERA and C. VOGT. Biocompatibility and degradation of LAE442-based magnesium alloys after implantation of up to 3.5 years in a rabbit model. *Acta Biomaterialia*. 2016, vol. 44, pp. 355–365. 10.1016/j.actbio.2016.08.002

[9] RÖSSIG, C., N. ANGRISANI, P. HELMECKE, S. BESDO, J.-M. SEITZ, B. WELKE, N. FEDCHENKO, H. KOCK and J. REIFENRATH. In vivo evaluation of a magnesium-based degradable intramedullary nailing system in a sheep model. *Acta Biomaterialia*. 2015, vol. 25, pp. 369–383. 10.1016/j.actbio.2015.07.025

[10] OSHIBE, N., E. MARUKAWA, T. YODA and H. HARADA. Degradation and interaction with bone of magnesium alloy WE43 implants: A long-term follow-up in vivo rat tibia study. *Journal of Biomaterials Applications*. 2019, vol. 33, no. 9, pp. 1157–1167. 10.1177/0885328218822050

[11] ULLMANN, B., J. REIFENRATH, J.-M. SEITZ, D. BORMANN and A. MEYER-LINDENBERG. Influence of the grain size on the in vivo degradation behaviour of the magnesium alloy LAE442. *Proceedings of the Institution of Mechanical Engineers. Part H, Journal of engineering in medicine*. 2013, vol. 227, no. 3, pp. 317–326. 10.1177/0954411912471495

[12] JIANG, J., A. MA, N. SAITO, Z. SHEN, D. SONG, F. LU, Y. NISHIDA, D. YANG and P. LIN. Improving corrosion resistance of RE-containing magnesium alloy ZE41A through ECAP. *Journal of Rare Earths*. 2009, vol. 27, no. 5, pp. 848–852. 10.1016/S1002-0721(08)60348-8

[13] HADZIMA, B., M. JANECEK, M. BUKOVINA and R. KRAL. Electrochemical properties of fine-grained AZ31 magnesium alloy. *International Journal of Materials Research*. 2009, vol. 100, no. 9, pp. 1213–1216. 10.3139/146.110186

[14] MINÁRIK, P., R. KRÁL and B. HADZIMA. Substantially Higher Corrosion Resistance in AE42 Magnesium Alloy through Corrosion Layer Stabilization by ECAP Treatment. *Acta Physica Polonica, A.* 2012, vol. 122, no. 3, pp. 614–617.

[15] SONG, D., A. MA, J. JIANG, P. LIN, D. YANG and J. FAN. Corrosion behavior of equal-channel-angular-pressed pure magnesium in NaCl aqueous solution. *Corrosion Science*. 2010, vol. 52, no. 2, pp. 481–490. 10.1016/j.corsci.2009.10.004

[16] MINARIK, P., R. KRAL, M. JANECEK and J. PESICKA. Evolution of the Microstructure, Mechanical Properties and Corrosion Resistance of AE21 Maggnesium Alloy after ECAP. In: *METAL 2013*: *METAL 2013 Conference Proceedings*. Brno, CZ: TANGER Ltd., 2013, p. 1546–1550. ISBN 978-80-87294-41-3.

[17] HALL, E.O. The Deformation and Ageing of Mild Steel: III Discussion of Results. *Proceedings of the Physical Society. Section B*. 1951, vol. 64, no. 9, pp. 747–753. 10.1088/0370-1301/64/9/303

[18] PETCH, N.J. The cleavage strength of polycrystals. *The Iron and Steel Institute*, vol. 174, 1953, no. 174, pp. 25–28.

[19] VALIEV, R.Z., Y. ESTRIN, Z. HORITA, T.G. LANGDON, M.J. ZECHETBAUER and Y.T. ZHU. Producing bulk ultrafine-grained materials by severe plastic deformation. *JOM*. 2006, vol. 58, no. 4, pp. 33–39. 10.1007/s11837-006-0213-7

[20] IWAHASHI, Y., J. WANG, Z. HORITA, M. NEMOTO and T.G. LANGDON. Principle of equal-channel angular pressing for the processing of ultra-fine grained materials. *Scripta Materialia*. 1996, vol. 35, no. 2, pp. 143–146. 10.1016/1359-6462(96)00107-8

[21] FURUKAWA, M., Z. HORITA, M. NEMOTO and T.G. LANGDON. Review: Processing of metals by equal-channel angular pressing. *Journal of Materials Science*. 2001, vol. 36, no. 12, pp. 2835–2843. 10.1023/A:1017932417043

[22] HORITA, Z., T. FUJINAMI and T.G. LANGDON. The potential for scaling ECAP: effect of sample size on grain refinement and mechanical properties. *Materials Science and Engineering: A*. 2001, vol. 318, nos. 1–2, pp. 34–41. 10.1016/S0921-5093(01)01339-9

[23] NAKASHIMA, K., Z. HORITA, M. NEMOTO and T.G. LANGDON. Development of a multi-pass facility for equal-channel angular pressing to high total strains. *Materials Science and Engineering: A*. 2000, vol. 281, nos. 1–2, pp. 82–87. 10.1016/S0921-5093(99)00744-3

[24] LEE, S. and T.G. LANGDON. Influence of Equal-Channel Angular Pressing on the Superplastic Properties of Commercial Aluminum Alloys. *MRS Online Proceedings Library*. 1999, vol. 601, p. 359. 10.1557/PROC-601-359

[25] KIM, W.J., C.W. AN, Y.S. KIM and S.I. HONG. Mechanical properties and microstructures of an AZ61 Mg Alloy produced by equal channel angular pressing. *Scripta Materialia*. 2002, vol. 47, no. 1, pp. 39–44. 10.1016/S1359-6462(02)00094-5

[26] KIM, W.J., S.I. HONG, Y.S. KIM, S.H. MIN, H.T. JEONG and J.D. LEE. Texture development and its effect on mechanical properties of an AZ61 Mg alloy fabricated by equal channel angular pressing. *Acta Materialia*. 2003, vol. 51, no. 11, pp. 3293–3307. 10.1016/S1359-6454(03)00161-7

[27] JANEČEK, M., S. YI, R. KRÁL, J. VRÁTNÁ and K.U. KAINER. Texture and microstructure evolution in ultrafine-grained AZ31 processed by EX-ECAP. *Journal of Materials Science*. 2010, vol. 45, no. 17, pp. 4665–4671. 10.1007/s10853-010-4675-1

[28] AGNEW, S.R., J.A. HORTON, T.M. LILLO and D.W. BROWN. Enhanced ductility in strongly textured magnesium produced by equal channel angular processing. *Scripta Materialia*. 2004, vol. 50, no. 3, pp. 377–381. 10.1016/j.scriptamat.2003.10.006

[29] LIN, H.K., J.C. HUANG and T.G. LANGDON. Relationship between texture and low temperature superplasticity in an extruded AZ31 Mg alloy processed by ECAP. *Materials Science and Engineering: A*. 2005, vol. 402, nos. 1–2, pp. 250–257. 10.1016/j.msea.2005.04.018

[30] LIU, T., Y.D. WANG, S.D. WU, R. LIN PENG, C.X. HUANG, C.B. JIANG and S.X. LI. Textures and mechanical behavior of Mg–3.3%Li alloy after ECAP. *Scripta Materialia*. 2004, vol. 51, no. 11, pp. 1057–1061. 10.1016/j.scriptamat.2004.08.007

[31] KRAJŇÁK, T., P. MINÁRIK, J. GUBICZA, K. MÁTHIS, R. KUŽEL and M. JANEČEK. Influence of equal channel angular pressing routes on texture, microstructure and mechanical properties of extruded AX41 magnesium alloy. *Materials Characterization*. 2017, vol. 123, pp. 282–293. 10.1016/j.matchar.2016.11.044

[32] WITTE, F., V. KAESE, H. HAFERKAMP, E. SWITZER, A. MEYER-LINDENBERG, C.J. WIRTH and H. WINDHAGEN. In vivo corrosion of four magnesium alloys and the associated bone response. *Biomaterials*. 2005, vol. 26, no. 17, pp. 3557–3563. 10.1016/j.biomaterials.2004.09.049

[33] WITTE, F., J. FISCHER, J. NELLESEN, H.-A. CROSTACK, V. KAESE, A. PISCH, F. BECKMANN and H. WINDHAGEN. In vitro and in vivo corrosion measurements of magnesium alloys. *Biomaterials*. 2006, vol. 27, no. 7, pp. 1013–1018. 10.1016/j.biomaterials.2005.07.037

[34] WITTE, F., J. FISCHER, J. NELLESEN, C. VOGT, J. VOGT, T. DONATH and F. BECKMANN. In vivo corrosion and corrosion protection of magnesium alloy LAE442. *Acta Biomaterialia*. 2010, vol. 6, no. 5, pp. 1792–1799. 10.1016/j.actbio.2009.10.012

[35] KRAUSE, A., N. von der HÖH, D. BORMANN, C. KRAUSE, F.-W. BACH, H. WINDHAGEN and A. MEYER-LINDENBERG. Degradation behaviour and mechanical properties of magnesium implants in rabbit tibiae. *Journal of Materials Science*. 2010, vol. 45, no. 3, pp. 624–632. 10.1007/s10853-009-3936-3

[36] THOMANN, M., Ch. KRAUSE, D. BORMANN, N. VON DER HÖH, H. WINDHAGEN and A. MEYER-LINDENBERG. Comparison of the resorbable magnesium alloys LAE442 und MgCa0.8 concerning their mechanical properties, their progress of degradation and

the bone-implant-contact after 12 months implantation duration in a rabbit model. *Materialwissenschaft und Werkstofftechnik*. 2009, vol. 40, nos. 1–2, pp. 82–87. 10.1002/mawe.200800412

[37] MASSALSKI, T.B. and H. OKAMOTO. *Binary alloy phase diagrams*. 2nd ed. Materials Park, Ohio: The Materials Information Society, 1990. ISBN 978-0-87170-403-0.

[38] TAYLOR, G.I. Plastic Strain in metals. *Journal of the Institute of Metals*. 1938, vol. 62, pp. 307–324.

[39] WITTE, F., N. HORT, C. VOGT, S. COHEN, K.U. KAINER, R. WILLUMEIT and F. FEYERABEND. Degradable biomaterials based on magnesium corrosion. *Current Opinion in Solid State and Materials Science*. 2008, vol. 12, nos. 5–6, pp. 63–72. 10.1016/j.cossms.2009.04.001

[40] ZHENG, Y.F., X.N. GU and F. WITTE. Biodegradable metals. *Materials Science and Engineering: R: Reports*. 2014, vol. 77, pp. 1–34. 10.1016/j.mser.2014.01.001

[41] XIN, Y., T. HU and P.K. CHU. In vitro studies of biomedical magnesium alloys in a simulated physiological environment: A review. *Acta Biomaterialia*. 2011, vol. 7, no. 4, pp. 1452–1459. 10.1016/j.actbio.2010.12.004

[42] DAVENPORT, A.J., C. PADOVANI, B.J. CONNOLLY, N.P.C. STEVENS, T.A.W. BEALE, A. GROSO and M. STAMPANONI. Synchrotron X-Ray Microtomography Study of the Role of Y in Corrosion of Magnesium Alloy WE43. *Electrochemical and Solid-State Letters*. 2006, vol. 10, no. 2, p. C5. 10.1149/1.2400727

[43] HÄNZI, A.C., P. GUNDE, M. SCHINHAMMER and P.J. UGGOWITZER. On the biodegradation performance of an Mg–Y–RE alloy with various surface conditions in simulated body fluid. *Acta Biomaterialia*. 2009, vol. 5, no. 1, pp. 162–171. 10.1016/j.actbio.2008.07.034

[44] BYUN, S.-H., H.-K. LIM, K.-H. CHEON, S.-M. LEE, H.-E. KIM and J.-H. LEE. Biodegradable magnesium alloy (WE43) in bone-fixation plate and screw. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*. 2020, vol. 108, no. 6, pp. 2505–2512. https://doi.org/10.1002/jbm.b.34582

[45] LI, N., C. GUO, Y.H. WU, Y.F. ZHENG and L.Q. RUAN. Comparative study on corrosion behaviour of pure Mg and WE43 alloy in static, stirring and flowing Hank's solution. *Corrosion Engineering, Science and Technology*. 2012, vol. 47, no. 5, pp. 346–351. 10.1179/1743278212Y.0000000006

[46] LU, C.L., H.Y. DONG, W. WANG and G. YANG. In Vivo and In Vitro Studies of Biodegradable WE43 Stent. *Applied Mechanics and Materials*. 2014, vol. 528, pp. 70–76. 10.4028/www.scientific.net/AMM.528.70

[47] FIGUEIREDO, R.B. and T.G. LANGDON. Grain refinement and mechanical behavior of a magnesium alloy processed by ECAP. *Journal of Materials Science*. 2010, vol. 45, no. 17, pp. 4827–4836. 10.1007/s10853-010-4589-y

[48] MASOUDPANAH, S.M. and R. MAHMUDI. Effects of rare-earth elements and Ca additions on the microstructure and mechanical properties of AZ31 magnesium alloy

processed by ECAP. *Materials Science and Engineering: A*. 2009, vol. 526, nos. 1–2, pp. 22–30. 10.1016/j.msea.2009.08.027

[49] MIYAHARA, Y., Z. HORITA and T.G. LANGDON. Exceptional superplasticity in an AZ61 magnesium alloy processed by extrusion and ECAP. *Materials Science and Engineering: A*. 2006, vol. 420, nos. 1–2, pp. 240–244. 10.1016/j.msea.2006.01.043

[50] MÁTHIS, K., J. GUBICZA and N.H. NAM. Microstructure and mechanical behavior of AZ91 Mg alloy processed by equal channel angular pressing. *Journal of Alloys and Compounds*. 2005, vol. 394, nos. 1–2, pp. 194–199. 10.1016/j.jallcom.2004.10.050

[51] JANEČEK, M., T. KRAJŇÁK, P. MINÁRIK, J. ČÍŽEK, J. STRÁSKÁ and J. STRÁSKÝ. Structural stability of ultra-fine grained magnesium alloys processed by equal channel angular pressing. *IOP Conference Series: Materials Science and Engineering*. 2017, vol. 194, no. 1, p. 012052. 10.1088/1757-899X/194/1/012052

[52] XU, Y.-K., H. MA, J. XU and E. MA. Mg-based bulk metallic glass composites with plasticity and gigapascal strength. *Acta Materialia*. 2005, vol. 53, no. 6, pp. 1857–1866. 10.1016/j.actamat.2004.12.036

[53] FARKAS, G., K. MÁTHIS, J. PILCH, P. MINÁRIK, P. LUKÁŠ and A. VINOGRADOV. Deformation behavior of Mg-alloy-based composites at different temperatures studied by neutron diffraction. *Materials Science and Engineering: A*. 2017, vol. 685, pp. 284–293. 10.1016/j.msea.2017.01.010

[54] KAWAMURA, Y. and M. YAMASAKI. Formation and Mechanical Properties of Mg97Zn1RE2 Alloys with Long-Period Stacking Ordered Structure. *Materials Transactions*. 2007, vol. 48, no. 11, pp. 2986–2992. 10.2320/matertrans.MER2007142

[55] STRÁSKÁ, J., P. MINÁRIK, S. ŠAŠEK, J. VESELÝ, J. BOHLEN, R. KRÁL and J. KUBÁSEK. Texture Hardening Observed in Mg–Zn–Nd Alloy Processed by Equal-Channel Angular Pressing (ECAP). *Metals*. 2020, vol. 10, no. 1, p. 35. 10.3390/met10010035

[56] LANGDON, T.G. Twenty-five years of ultrafine-grained materials: Achieving exceptional properties through grain refinement. *Acta Materialia*. 2013, vol. 61, no. 19, pp. 7035–7059. 10.1016/j.actamat.2013.08.018

[57] YANG, Q., B.L. XIAO, Q. ZHANG, M.Y. ZHENG and Z.Y. MA. Exceptional high-strain-rate superplasticity in Mg–Gd–Y–Zn–Zr alloy with long-period stacking ordered phase. *Scripta Materialia*. 2013, vol. 69, no. 11, pp. 801–804. 10.1016/j.scriptamat.2013.09.001

6. List of publications

[PM1] **P. Minárik**, R. Král, M. Janeček: Effect of ECAP processing on corrosion resistance of AE21 and AE42 magnesium alloys, Applied Surface Science 281 (2013), 44–48. 10.1016/j.apsusc.2012.12.096

[PM2] **P. Minárik**, R.Král, J. Pešička, S. Daniš, M. Janeček: Microstructure characterization of LAE442 magnesium alloy processed by extrusion and ECAP, Materials Characterization 112 (2016), 1–10. 10.1016/j.matchar.2015.12.002

[PM3] **P. Minárik**, J. Čížek, J. Veselý, P. Hruška, B. Hadzima, R. Král: Nanocrystalline aluminium particles inside Mg-4Li-4Al-2RE magnesium alloy after severe plastic deformation, Materials Characterization 127 (2017), 248–52. 10.1016/j.matchar.2016.12.021

[PM4] **P. Minárik**, R. Král, J. Čížek, F. Chmelík: Effect of different c/a ratio on the microstructure and mechanical properties in magnesium alloys processed by ECAP, Acta Materialia 107 (2016): 83–95. 10.1016/j.actamat.2015.12.050

[PM5] **P. Minárik**, E. Jablonská, R. Král, J. Lipov, T. Ruml, C. Blawert, B. Hadzima, F. Chmelík: Effect of equal channel angular pressing on in vitro degradation of LAE442 magnesium alloy, Materials Science and Engineering: C 73 (2017), 736–42. 10.1016/j.msec.2016.12.120

[PM6] **P. Minárik**, J. Veselý, R. Král, J. Bohlen, J. Kubásek, M. Janeček, J. Stráská: Exceptional mechanical properties of ultra-fine grain Mg-4Y-3RE alloy processed by ECAP, Materials Science and Engineering: A 708 (2017), 193–98. 10.1016/j.msea.2017.09.106

[PM7] **P. Minárik**, J. Veselý, J. Čížek, M. Zemková, T. Vlasák, T. Krajňák, J. Kubásek, R. Král, D. Hofman, J. Stráská: Effect of secondary phase particles on thermal stability of ultra-fine grained Mg-4Y-3RE alloy prepared by equal channel angular pressing, Materials Characterization 140 (2018), 207–16. 10.1016/j.matchar.2018.04.006

[PM8] T. Vávra, **P. Minárik**, J. Veselý, R. Král: Excellent Superplastic Properties Achieved in Mg–4Y–3RE Alloy in High Strain Rate Regime, Materials Science and Engineering: A 784 (2020), 139314. 10.1016/j.msea.2020.139314

[PM9] **P. Minárik**, M. Zemková, J. Veselý, J. Bohlen, M. Knapek, R. Král: The Effect of Zr on Dynamic Recrystallization during ECAP Processing of Mg-Y-RE Alloys, Materials Characterization 174 (2021), 111033.

7. Reprints of the selected papers