Kovove Mater. 59 2021 315–319
DOI: 10.4149/km_2021_5_315

Hot extrusion of magnesium/hydroxyapatite composites prepared by powder metallurgy

M. Čavojský[1]*, V. Nagy-Trembošová[1,2], N. Beronská[1], M. Nosko[1]

[1]*Institute of Materials and Machine Mechanics, Slovak Academy of Sciences, Dúbravská cesta 9, 845 13 Bratislava, Slovak Republic*
[2]*Faculty of Materials Science and Technology in Trnava, STU, Jána Bottu 25, 917 24 Trnava, Slovak Republic*

Received 24 August 2021, received in revised form 7 September 2021, accepted 20 September 2021

Abstract

Magnesium biocompatibility and mechanical properties comparable with those of bones predetermine magnesium and materials based on magnesium for application as biodegradable implants. Pure magnesium usually has very poor properties that need to be improved. These properties can be improved by various alloying elements. However, these elements are usually not biocompatible. An alternative way to improve both mechanical and corrosion properties is by using composite materials. The presence of hydroxyapatite in magnesium should improve the mechanical properties and, at the same time, reduce the rate of corrosion by the barrier effect. This paper focuses on Mg/HA composite materials prepared from pure magnesium powders and hydroxyapatite (HA) powders. Powders were consolidated via cold compaction and subsequently directly extruded. The microstructure was revealed through SEM-EDS, mechanical properties were determined by tensile test. The corrosion resistance of composites was evaluated by immersion and electrochemical measurements in simulated body fluid.

K e y w o r d s: magnesium, hydroxyapatite, powder metallurgy, biocompatibility, microstructure, mechanical properties

1. Introduction

Nowadays, magnesium and its alloys are currently very attractive as a potential material for biodegradable bone implants, considering their mechanical properties. Magnesium density is the lowest compared to other structural metals, and its Young's modulus is actually near that of bone. Also, it demonstrates a degradable nature when putting into an environment of living cells [1–3]. Low density and high specific strength make Mg alloys attractive for applications to bring high cost and energy savings [4–7]. Nevertheless, rapid corrosion, low strength, and toxic ions deposited by aluminum and other heavy elements in some magnesium alloys have limited their use. To use this material for medical applications, it is necessary to solve these problems [8]. Many works already described Mg or Mg alloys as a new class of degradable biomaterials for orthopaedic implantations [9–11].

Hydroxyapatite (HA) has received increasing attention in the production of bone grafting materials and dental prosthetics. When comparing all calcium phosphate-containing bioceramics, HA is the most applied for medical purposes due to its biocompatibility with a living organism and a chemical composition similar to bone. In fact, biocomposite materials could achieve different mechanical and biological properties [12–14]. Furthermore, the contact between the biocomposite and the surrounding tissue may be a function of the components [15–16]. Therefore, HA can be a suitable choice for the production of Mg/HA nanocomposites to achieve Mg and HA properties simultaneously.

One of the main advantages of biodegradable implants is eliminating the subsequent operation to remove the implant after sufficient tissue healing [17–18]. In general, the elastic modulus difference can lead to the implant carrying more of the load and causing stress shielding of the bone [19]. This biomedical incompatibility can result in critical clinical issues,

*Corresponding author: tel.: +421232401041; e-mail address: miroslav.cavojsky@savba.sk

such as early implant loosening, damage to the healing process, skeletal thickening, and chronic inflammation [20]. In addition, magnesium implants have been shown to stimulate new bone formation when implanted as bone supplements [17]. Research in the suitability of magnesium and its alloys as implants has a long history [17] and is booming at present [21]. But the advantages of Mg combined with its non-toxicity and biodegradability do not match its mechanical performance, although its modulus is close to that of natural bone. An alternative way of enhancing mechanical and corrosion properties is using metal matrix composites [22]. Corrosion and mechanical properties can be adjusted by the volume fraction of reinforcement. Many magnesium matrix composites were primarily investigated with hydroxyapatite (HA) reinforcement. Improvement of mechanical and corrosion properties was confirmed [23].

It is crucial to choose the proper preparation method for composite material. The ideal method for the preparation of composite materials seems to be powder metallurgy [24]. It offers few methods for effective powder homogenization and powder compacting [25]. Extrusion is the standard way of processing magnesium-based materials [26]. Extrusion suppresses porosity, increases homogeneity, and is usually associated with the recrystallization process [27]. Therefore composite materials with 3, 6, and 9 wt.% of hydroxyapatite were prepared by extrusion. Pure magnesium was prepared in the same way for the comparison. This paper is focused on manufacturing the profiles through the powder metallurgy (PM) route to analyze the microstructure and mechanical properties. The main goal is to analyze the corrosion resistance possibility of this material for use in biocompatible applications.

2. Experimental

In the present paper, Mg powder of 99.96 % purity made by gas atomization in Ar atmosphere and hydroxyapatite (HA) powder of 99.9 % purity were used for the study. Composites with 3, 6, and 9 wt.% of reinforcement were prepared using magnesium (Fig. 1a) with mean particle size $\sim 40\,\mu m$ and hydroxyapatite (Fig. 1b) with mean particle size $\sim 50\,\mu m$. The chemical analysis was performed using fluorescence ARL 9400 XP spectrometer with Rh cathode and 4 kW tube. Impurities including Zn – 0.076 wt.%, Cu – 0.01 wt.%, Fe – 0.079 wt.%, and Ni – 0.001 wt.% were determined in as received Mg powder. Microstructures of powders were analyzed using a field emission scanning electron microscope (FEG-SEM7600F, JEOL, Japan) equipped with an energy dispersive spectrometer (EDS, Oxford Instruments X-Max 50 mm^2). For the investigation of extruded samples, metallographic preparation was carried out.

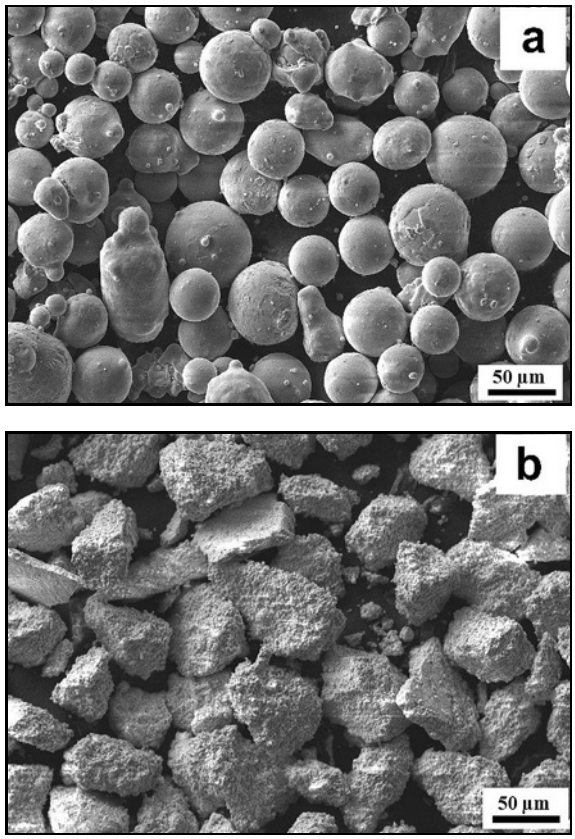

Fig. 1. SEM images representing Mg atomized powders (a) and hydroxyapatite powders (b).

Powders of Mg and HA were mixed in a turbula mixer for 20 min. Green compacts of composite materials, 30 mm in diameter and 60 mm in height, were prepared by cold isostatic pressing (CIP) at 200 MPa. Direct extrusion (DE) was performed at an average ram speed of $\sim 0.2\,mm\,s^{-1}$ using an extrusion ratio of $R = 16:1$. Prior to extrusion, green compacts were heated to 390 ℃ for 15 min. The final extruded rods were 7.5 mm in diameter. Mechanical properties in tension were measured on tensile bars with a gauge of ø 5–30 mm using a ZWICK testing machine at a cross-ram speed of $6 \times 10^{-4}\,min^{-1}$ according to STN EN ISO 6892-1 standard. Vickers hardness measurements at 5 kg and 10 s were performed. Measurement was performed parallel to the extrusion direction. Corrosion tests were performed in simulated body fluid (SBF) at 37 ℃ for 7 days. The simulated body fluid reflects all inorganic compounds of human plasma. Samples were rinsed after exposure, and corrosion products were removed by a solution of $200\,g\,L^{-1}$ CrO_3, $10\,g\,L^{-1}$ $AgNO_3$, $20\,g\,L^{-1}$ $Ba(NO_3)_2$. The corrosion rate was calculated every day from weight change after removing the corrosion products.

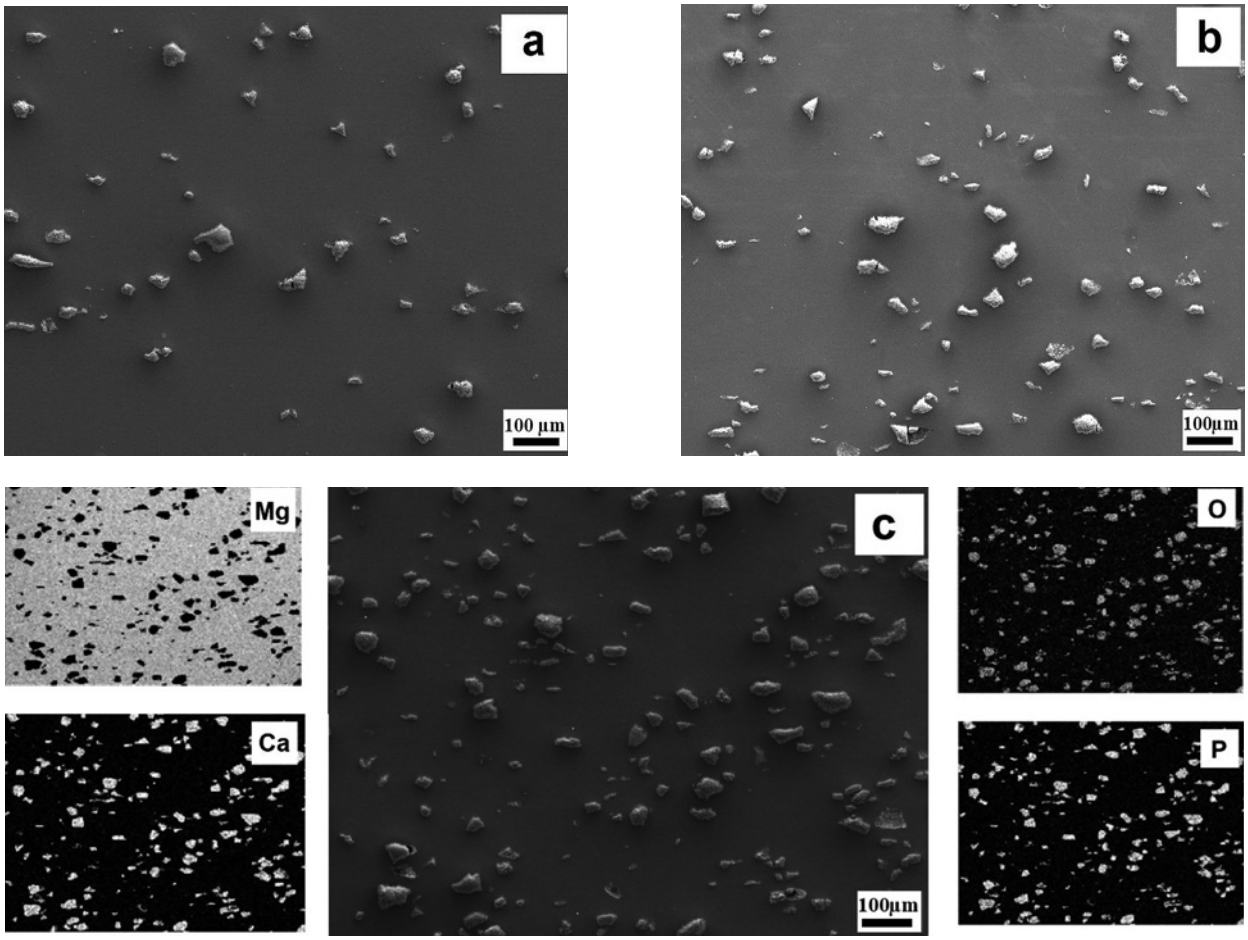

Fig. 2. Composite materials prepared by extrusion of powders: (a) Mg-3HA, (b) Mg-6HA, (c) Mg-9HA, and EDS map revealing the distribution of O, Mg, P and Ca.

3. Results and discussion

3.1. Microstructure

The structures of extruded composites as revealed by SEM are shown in Figs. 2a–c. As can be seen, particles of HA are homogeneously distributed in the Mg matrix. Such distribution should positively affect mechanical properties, and they may effectively obstruct the grain growth of the Mg matrix during extrusion. Another advantage of extrusion is friction between particles during this process, which disrupts oxide shells of magnesium powders [23].

A homogeneous microstructure was observed in all composite materials (Figs. 2a–c). The inhomogeneous structure did not occur even with higher amounts of HA. Homogeneous distribution of the particles was observed in the longitudinal section.

3.2. Mechanical properties

The tensile strength of composite material was measured and was compared with pure magnesium prepared the same way as a composite material as presented in Fig. 3. The yield strength of the composite materials gradually increased up to 2 times the value at 6 and 9 wt.% HA as the yield strength of pure magnesium. From the tensile and yield strength (Fig. 3), the increase of ultimate tensile strength can be seen

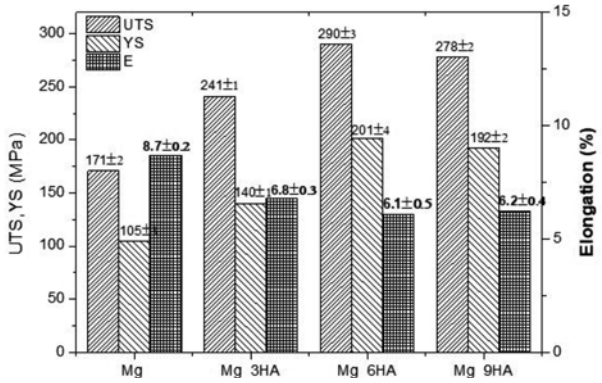

Fig. 3. Mechanical properties (UTS, YS, and elongation) of the extruded Mg and composite materials Mg-xHA.

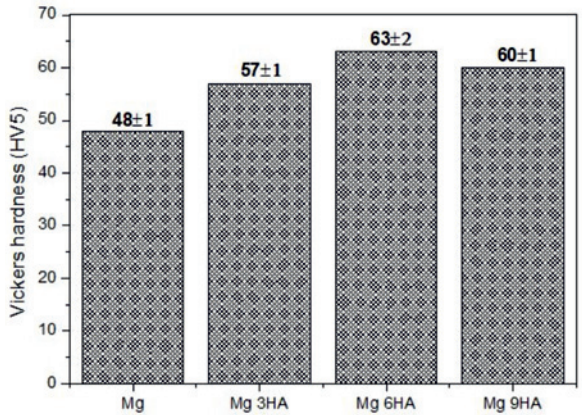

Fig. 4. Vickers hardness of the cross-section of the pure Mg and Mg-xHA composites.

up to 6 % of HA, and the elongation remains roughly at the same values.

The inferior mechanical properties of a sample with 9 % of HA can be due to the higher amount of hydroxyapatite particles, decreasing plasticity of the product. Khanra et al. [28] prepared Mg-5HA composites by the classical casting method. Composites were homogenized by melting, and cast ingots were subsequently extruded. As a result, they reached YS and UTS values of 100 and 200 MPa, respectively, which is much lower than those in the present paper. In this work, we were able to prepare composite materials with improved mechanical properties due to the homogeneous structure.

The hardness was measured and compared with pure magnesium. Hardness values of the cross-section of the samples are presented in Fig. 4. It is evident that values are increasing by adding up to 6 wt.% HA in the Mg matrix. Also, this trend in hardness values is in accordance with the tensile tests accomplished. This is primarily due to the significantly higher hardness of hydroxyapatite compared to magnesium.

Since the mechanical properties of composites were significantly improved with respect to pure magnesium, Mg-xHA PM material might be regarded as a promising candidate for biocompatible and biodegradable material applications. Moreover, the effect of the corrosion rate and thus the potential of the material with regards to the biodegradable rate have to be thoroughly studied.

3.3. Corrosion behavior

Corrosion behavior was studied by immersion tests in simulated body fluid (SBF) at 37 ℃ for one week. Each sample was immersed in the closed container in approximately 300 ml of SBF solution. Final corrosion rates were calculated from changes in the mass and concentration of released magnesium ions in the corrosion environment. Pure magnesium was characterized by a corrosion rate V_{corr} (0.879 mg cm^{-2} day^{-1}). The highest corrosion resistance was obtained for composite materials with 6 wt.% HA, which reached V_{corr} (0.548 mg cm^{-2} day^{-1}). A slightly higher corrosion rate of the extruded alloy is associated with a higher amount of 9 wt.% HA. Hydroxyapatite, which is known to increase corrosion resistance by incorporating HA in protective oxide layers which are formed during corrosion, was characterized by a corrosion rate V_{corr} (0.624 mg cm^{-2} day^{-1}). The corrosion rate of the pure Mg sample extruded from the as-cast state is characterized by the highest corrosion rate, almost one-third higher compared to that of the composite material. Nevertheless, the high corrosion rate was caused by numerous MgO phases, which acted as cathode areas and accelerated the corrosion by microgalvanic cells [25].

4. Conclusions

Mg/xHA (x = 0, 3, 6, 9 wt.%) composites were prepared by powder metallurgy methods including extrusion. Based on the characterization of the mechanical properties and the observation of the structure, a suitable amount of HA addition was determined to be 6 wt.%, and a method for preparing Mg-HA composites was specified. This process involves homogenization, pressing of the green compact, and extrusion at 390 ℃. The samples prepared by this method were characterized by a uniform structure and improved mechanical properties. Microstructural analysis shows that a homogeneous microstructure was achieved in all composites. The specimen presenting the highest strength is the Mg-6HA composite which offers a UTS of $\sim$ 290 MPa. The elongation of this composite drops slightly to 6.1 % from 6.8 % for the Mg-3HA composite. All composites show roughly the same elongation. In sum, optimum mechanical properties belong to the Mg-6HA composite, and by adding more HA, mechanical properties deteriorate. Also, the highest value of Vickers hardness appears for the sample containing 6 wt.% HA, and tensile test results were confirmed. The highest corrosion resistance was obtained for composite materials with 6 wt.%, which reached V_{corr} (0.548 mg cm^{-2} day^{-1}). The best combination of mechanical and corrosion properties was obtained for the sample with 6 wt.% of HA.

Acknowledgement

This study was elaborated within the project "VEGA 2/0098/19 – Study of the use of pure magnesium powders for the preparation of biodegradable materials ".

References

[1] F. Witte, V. Kaese, H. Haferkamp, E. Switzer, A. Meyer-Lindenberg, C. J. Wirth, H. Windhagen, In vivo corrosion of four magnesium alloys and the associated bone response, Biomaterials 26 (2005) 3557–3563. doi:10.1016/j.biomaterials.2004.09.049

[2] L. Xu, G. Ju, E. Zhang, F. Pan, K. Yang, In vivo corrosion behavior of Mg-Mn-Zn alloy for bone implant application, J. Biomed. Mater. Res. A 83 (2007) 703–711. doi:10.1002/jbm.a.31273

[3] G. Xiong, Y. Nie, D. Ji, J. Li, Ch. Li, W. Li, Y. Zhu, H. Lou, Y. Wan, Characterization of biomedical hydroxyapatite/magnesium composites prepared by powder metallurgy assisted with microwave sintering, Curr. Appl. Phys. 16 (2016) 830–836. doi:10.1016/j.cap.2016.05.004

[4] B. Mordike, T. Ebert, Magnesium: Properties – applications – potential, Mater. Sci. Eng. A 302 (2001) 37–45. doi:10.1016/S0921-5093(00)01351-4

[5] G. Cole, Magnesium vision 2020 – a north American automotive strategic vision for magnesium, Proceedings of the IMA, International Magnesium Association, McLean, VA, USA, 2007, p. 13.

[6] M. Easton, A. Beer, M. Barnett, C. Davies, G. Dunlop, Y. Durandet, S. Blacket, T. Hilditch, P. Beggs, Magnesium alloy applications in automotive structures, JOM 60 (2008) 57–62. doi:10.1007/s11837-008-0150-8

[7] T. M. Pollock, Weight loss with magnesium alloys, Science 328 (2010) 986–987. doi:10.1126/science.1182848

[8] B. Zhang, Y. Hou, X. Wang, Y. Wang, L. Geng, Mechanical properties, degradation performance and cytotoxicity of Mg-Zn-Ca biomedical alloys with different compositions, Mater. Sci. Eng. C 31 (2011) 1667–1673. doi:10.1016/j.msec.2011.07.015

[9] L. Yang, Y. Huang, Q. Peng, F. Feyerabend, K. U. Kainer, R. Willumeit, N. Hort, Mechanical and corrosion properties of binary Mg-Dy alloys for medical applications, Mater. Sci. Eng. B 179 (2011) 1827–34. doi:10.1016/j.mseb.2011.02.025

[10] D. Liu, D. Yang, X. Li, S. Hu, Mechanical properties, corrosion resistance and biocompatibilities of degradable Mg-RE alloys: A review, J. Mater. Res. Technol. 8 (2019) 1538–1549. doi:10.1016/j.jmrt.2018.08.003

[11] R. Radha, D. Sreekanth, Insight of magnesium alloys and composites for orthopedic implant applications – A review, Journal of Magnesium and Alloys 5 (2017) 286–312. doi:10.1016/j.jma.2017.08.003

[12] E. Salernitano, C. Migliaresi, Composite materials for biomedical applications: A review, J. Appl. Biomater. Biomech. 1 (2003) 3–18. doi:10.1177/228080000300100102

[13] M. F. Vassal, J. Nunes-Pereira, S. P. Miguel, I. J. Correia, A. P. Silva, Microstructural, mechanical and biological properties of hydroxyapatite-$CaZrO_3$ biocomposites, Ceram. Int. A 45 (2019) 8195–8203. doi:10.1016/j.ceramint.2019.01.122

[14] M. Biesuz, A. Galotta, A. Motta, M. Kermani, S. Grasso, J. Vontorová, V. Tyrpekl, M. Vilémová, V. M. Sglavo, Speedy bioceramics: Rapid densification of tricalcium phosphate by ultrafast high-temperature sintering, Mater. Sci. Eng. C 127 (2021) 112246. doi:10.1016/j.msec.2021.112246

[15] S. Chen, Y. Shi, X. Zhang, J. Ma, 3D printed hydroxyapatite composite scaffolds with enhanced mechanical properties, Ceram. Int. 45 (2019) 10991–10996. doi:10.1016/j.ceramint.2019.02.182

[16] X. Fan, Preparation and performance of hydroxyapatite/Ti porous biocomposite scaffolds, Ceram. Int. 45 (2019) 16466–16469. doi:10.1016/j.ceramint.2019.05.178

[17] M. P. Staiger, A. M. Pietak, J. Huadmai, G. Dias, Magnesium and its alloys as orthopaedic biomaterials: A review, Biomaterials 27 (2006) 1728–1734. doi:10.1016/j.biomaterials.2005.10.003

[18] S. Fare, Q. A. Ge, M. Vedani, G. Vimercati, D. Gastaldi, F. Migliavacca, L. Petrini, S. Trasatti, Evaluation of material properties and design requirements for biodegradable magnesium stents, Revista Matéria 15 (2010) 103–112. http://www.materia.coppe.ufrj.br/sarra/artigos/artigo11202

[19] C. K. Seal, K. Vince, M. A. Hodgson, Biodegradable surgical implants based on magnesium alloys – A review of current research, IOP Conference Series: Materials Science and Engineering 4 (2009) 12011–12014. doi:10.1088/1757-899X/4/1/012011

[20] M. Salahshoor, Y. B. Guo, Biodegradable orthopaedic magnesium-calcium (MgCa) alloys, processing, and corrosion performance, Materials 5 (2012) 135–155. doi:10.3390/ma5010135

[21] S. Virtanen, Biodegradable Mg and Mg alloys: Corrosion and biocompatibility, Mater. Sci. Eng. B 176 (2011) 1600–1608. http://dx.doi.org/10.1016/j.mseb.2011.05.028

[22] G. L. Song, A. Atrens, Corrosion mechanisms of magnesium alloys, Advanced Engineering Materials 1 (1999) 11–33. doi:10.1002/(SICI)1527-2648(199909)1:1<11::AID-ADEM11>3.0.CO;2-N

[23] D. Dvorsky, J. Kubasek, D. Vojtěch, Hydroxyapatite in materials for medical applications, Manufacturing Technology 15 (2015) 969–973. doi:10.21062/ujep/x.2015/a/1213-2489/MT/15/6/969

[24] J. Kubásek, D. Dvorský, M. Čavojský, D. Vojtěch, N. Beronská, M. Fousová, Superior properties of Mg-4Y-3RE-Zr alloy prepared by powder metallurgy, Journal of Materials Science & Technology 33 (2016) 652–660. doi:10.1016/j.jmst.2016.09.019

[25] M. Čavojský, V. Trembošová, N. Beronská, Š. Nagy, M. Nosko, Microstructure and mechanical properties of extruded profiles made from pure magnesium powders, Kovove Mater. 57 (2019) 371–376. doi:10.4149/km_2019_6_371

[26] D. Dvorsky, J. Kubasek, D. Vojtech, M. Cavojsky, Structure and mechanical properties of WE43 prepared by powder metallurgy route, Manufacturing Technology 16 (2016) 896–902. doi:10.21062/ujep/x.2016/a/1213-2489/MT/16/5/896

[27] J. Kubasek, D. Vojtěch, D. Dvorský, The effect of thermo-mechanical processing on the structure, static mechanical properties and fatigue behavior of pure Mg, Materiali in Tehnologije 51 (2017) 289–296. doi:10.17222/mit.2016.029

[28] A. K. Khanra, H. C. Jung, K. S. Hong, K. S. Shin, Comparative property study on extruded Mg-HAP and ZM61-HAP composites, Materials Science and Engineering A 527 (2010) 6283–6288. doi:10.1016/j.msea.2010.06.031