Characterisation of structure, mechanical and corrosion properties of pure magnesium prepared by powder metallurgy route

Drahomír Dvorský¹,², Jiří Kubásek¹, Dalibor Vojtěch¹

¹Department of Metals and Corrosion Engineering, Faculty of Chemical Technology, University of Chemistry and Technology Prague, Technická 5 166 28 Praha 6 – Dejvice, Czech Republic
²Institute of Physics, Czech Academy of Science, Prague, Na Slovance 1999/2 182 21 Praha 8, Czech Republic
dvorskyd@vscht.cz

Abstract. Powder metallurgy is a progressive method for materials production. Final products are usually characterised by improved strength and corrosion properties compared to materials prepared by conventional methods like casting and subsequent thermomechanical processing. The presented work studies the effect of extrusion temperature on the microstructure and properties of products prepared from pure Mg powder. It has been observed that higher extrusion temperature led to the formation of larger grains and massive oxides at interparticle boundaries. Tensile yield strength, compressive, and tensile ultimate strengths were increased at the cost of lower plasticity. The observed mechanical properties were mainly affected by texture, oxides, and grain size. The high corrosion rate was attributed to the presence of a relatively high amount of oxides and impurities which facilitate localized corrosion.

1. Introduction
Magnesium is a light metal suitable for application in the automotive and aviation industry. Its mechanical and corrosion properties are also advantageous for application in medicine as a material for biodegradable implants [1]. Such materials should have appropriate mechanical and corrosion properties which can be improved by alloying. However, in the case of biodegradable implants, alloying elements should also be biocompatible. The most advanced used materials for medicine are alloys with rare earth (RE) elements [2]. Even though the cytotoxicity tests and in vivo tests revealed no harmful effect of those elements, the long-term impact of those elements is yet unknown. Therefore, there is an effort to reduce the amount of alloying elements or to use pure Mg. Nevertheless, pure Mg is prone to fast corrosion if dangerous impurities like Fe, Ni, or Cu are present in the amount exceeding allowed limits (Fe: 35–50 ppm, Ni: 20–50 ppm, Cu: 100–300 ppm) [3].

The mechanical and corrosion properties might be improved by the processing of the material. Powder metallurgy seems to be a suitable way to produce such materials. It was investigated that materials prepared by powder metallurgy exert superior mechanical and corrosion properties compared with casted ingot [4-6]. Especially, if it is combined with thermomechanical processing such as extrusion. Material is severely deformed and dynamic recrystallization may occur due to the elevated temperature. The final desired structure is characterised by fine uniaxial grains [7]. Nevertheless, extrusion of materials with hcp structure may resolve in the specific texture in the material. Magnesium is usually characterised with typical basal texture for rolling or fibre texture.
after extrusion, which causes anisotropy of mechanical properties [8, 9]. The orientation of basal planes of magnesium hexagons is parallel to the extrusion direction after extrusion. This orientation is favorable for the twinning in compression and unfavorable for the twinning in tension. Twinning requires less energy to occur in textured materials than the slip mechanism in the unfavorably oriented basal planes, and therefore, there are great differences in the measured compressive and tensile yield strengths of materials with strong texture [9, 10].

This paper deals with the effect of extrusion temperature on the final mechanical and corrosion properties of powder metallurgy products.

2. Materials and methods

2.1. Material preparation
Pure Mg atomized powder (90 ppm of Fe, 20 ppm of Cu, 10 ppm of Ni – identified by ICP-MS Elan DRC-e) with round-shaped particles was obtained from the commercial supplier with the particle size ranging between 0.1 and 250 µm. The powder size distribution is in the figure 1. The powder was pressed on the universal LabTEST 250SP1-VM machine with a pressure of 255 MPa for 5 min. The green compact sample was then extruded at the same machine at 200 °C, 300 °C, 400 °C, and 500 °C. The final rods had 6 mm in diameter. The extrusion ratio was 10 and the extrusion rate 5 mm·min⁻¹.

2.2. Microstructure characterisation
Characterisation of the samples was performed using a TescanVEGA3 LMU scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS). Samples were ground on the SiC papers P80-P4000, afterward, they were polished on diamond pastes D2 and D0.7. The final polishing was performed on the Eposil F suspension. Samples were etched in the solution of 30 ml of acetic acid, 10 ml of nitric acid, 40 ml of water, and 120 ml of ethanol. EBSD analysis was performed on the same microscope with NordlysMax electron back-scattered diffraction (EBSD) detector, and AZtecHKL software). Parameters selected for EBSD analysis: working distance of 15 mm, accelerating voltage of 20 kV, dwell-exposure time of 0.26 s/pt, step size of 0.25 µm.

2.3. Mechanical properties
Compressive and tensile properties were measured using LabTest 5.250SP1-VM at room temperature at a strain rate of 0.001 s⁻¹. Cylindrical samples with a diameter of 5 mm and 7.5 mm high were used for
Compressive tests. Compressive yield strength (CYS) and ultimate compressive strength (UCS) were determined from compressive curves. Tensile tests were performed on dog bone specimens with a gauge length of 25 mm and diameter equal to 3.5 mm. Tensile yield strength (TYS), ultimate tensile strength (UTS), and elongation to fracture (A) were determined from compressive curves. Three measurements were performed for each material.

2.4. Corrosion test
Corrosion behaviour was studied in the simulated body fluid SBF according to Müller [11]. 100 ml of SBF was used for 1 cm² of the sample surface. Samples were exposed to SBF in non-hermetically closed plastic containers for 14 days at 37 °C. The corrosion rate was evaluated based on the weight changes after the removal of corrosion products in the solution of 200 g/l CrO₃, 10 g/l AgNO₃, 20 g/l Ba(NO₃)₂. The difference in weight was divided by density, exposed surface, and number of days of exposure and multiplied by 365 in order to obtain corrosion rate in mm·a⁻¹. Three measurements were performed for each material.

3. Results and discussion

3.1. The microstructures
Microstructures of extruded products are displayed in figure 2. All materials were characterised by rows parallel to the extrusion direction containing oxides. Generally, the porosity of the material after extrusion is close to zero according to the image analysis, however, some oxides might be removed during polishing and etching which created some pores during metallography preparation. Present rows represent the original surface of Mg particles, therefore, the powder particles were deformed and stretched in the extrusion direction. Those borders were not eliminated probably due to the low extrusion ratio. Cavojsky et al. [12] prepared pure Mg with an extrusion ratio of 16 and they were able to disturb original powder particles. Nevertheless, oxides in the structure were ordered in rows parallel to the extrusion direction. One can see that the grain size increases with the extrusion temperature as well as the amount of oxides in the structure. Similar results were observed by Perez et al. [13] who prepared pure Mg with an extrusion ratio of 18 at various extrusion temperatures. Oxides were originally on the surface of each particle in a small amount, which is visible on the sample extruded at 200 °C. However, during heating before extrusion, the residual air between particles of green compact increased the amount of oxides on the surface of the original particles.

![Figure 2: Microstructures of the extruded powders and IPF maps in the extrusion direction of extruded products.](image)

EBSD analysis revealed information about the grain size and grain orientation in the material. The average grain sizes were 2.7 µm, 6.4 µm, 11.7 µm, and 23.4 µm for materials extruded at 200 °C,
300 °C, 400 °C, and 500 °C, respectively. Those are similar or slightly smaller grain sizes compared to those prepared at the equal extrusion temperature by powder metallurgy [12, 13]. In comparison with materials prepared by extrusion of an ingot, there is a lower grain size of powder metallurgy products [14, 15]. Figure 2 represents the results of EBSD analysis at the two extreme conditions (extrusion at 200 °C and 500 °C). White areas in figure 2 represent unindexed points due to the defects or oxides while red linear grain is probably sign of twinning. One can see a large difference in grain size and primarily in grain orientation. There is a five times stronger basal texture in the case of extrusion at 500 °C compared to the extrusion at 200 °C. The same results were measured by Perez et al. [13] who performed extrusion temperatures of 250 °C, 325 °C, 400 °C, and 450 °C. The strong texture was observed also by Cavojsky et al. [12] for powder extruded at 390 °C and even by Kubasek et al. [14] for extruded ingot at 200 °C.

3.2. Mechanical properties

Compressive (solid line) and tensile (dash line) properties are summarized in figure 3 and table 1. At first sight, there are visible some trends, that the compressive yield strength (CYS) and plasticity (A) decreases with higher extrusion temperature. Contrary, the ultimate compressive strength (UCS) and tensile yield strength (TYS) increased with the extrusion temperature.

Mechanical properties of pure Mg are affected by several factors such as grain size, texture strength, and volume and character of oxides. There was an increased amount of oxides with higher extrusion temperature, which may result in the enhancement of strengths. On the contrary, its presence deteriorates plasticity. Smaller grains shall exert the improvement of yield strengths according to the Hall-Patch relation. Therefore, higher extrusion temperature should lead to lower CYS and TYS. This is true only for the CYS as there is a third factor – texture. The presence of texture may justify the anisotropy of mechanical properties, as there are great differences between CYS and TYS values of prepared products. Moreover, there are contradictory trends in CYS and TYS related to the extrusion temperature.

The strongest texture was measured for the sample extruded at 500 °C as well as the greatest difference between CYS and TYS, which was 130 MPa. This is caused by preferential grain orientation which is favourable for the twinning mechanism in compression. Moreover, a larger grain size intensifies the twinning mechanism. This is visible on the compressive curve (black solid line in figure 3), which has the typical “S” shape with a well visible area of strengthening. Twinning requires less energy in textured materials than a slip mechanism in a unfavourably oriented basal planes, and therefore, the measured CYS is relatively low. On the other hand, tensile yield strength is increased as the twinning mechanism is suppressed in tension due to the presented texture, and the deformation is primarily provided by the slip mechanism. Large grains have a long slipping distance, which allows strengthening in tension as well, which is also visible on the tensile curve (dash black line in figure 3).

In the case of extrusion at the lowest temperature, there was CYS higher than TYS. Such behaviour is related to the defects or inhomogeneities in a material that affects more tensile properties than compressive. Relatively small grains together with weaker specific texture are not suitable for twinning with low activation energy and consequently, the value of CYS is increased. Low amount of oxides, lower specific texture strength manifest in lower TYS and better ductility for sample extruded at 200 °C.

The obtained mechanical properties are better than properties of as-casted materials [16] and even slightly better than extruded ingot [14]. This is associated with the grain size and also by MgO reinforcement, which is not present in the casted ingot. On the contrary, other authors achieved higher strengths [12, 13], however also lower plasticity, which can be contributed to the stronger texture of the material. A higher strength might also be connected with a higher extrusion ratio. Milling of the powder prior to extrusion resulted in higher strengths, lower anisotropy of mechanical properties and slightly lower ductility [17].
Figure 3: Compressive (solid line) and tensile (dash line) curves.

Table 1: Mechanical properties of prepared samples.

|       | Ex 200 °C | Ex 300 °C | Ex 400 °C | Ex 500 °C |
|-------|-----------|-----------|-----------|-----------|
| CYS [MPa] | 151 ± 2   | 112 ± 2   | 76 ± 1    | 70 ± 1    |
| UCS [MPa]  | 200 ± 3   | 210 ± 8   | 235 ± 9   | 382 ± 10  |
| TYS [MPa]  | 89 ± 4    | 132 ± 3   | 163 ± 4   | 174 ± 5   |
| UTS [MPa]  | 147 ± 8   | 168 ± 7   | 187 ± 9   | 233 ± 9   |
| A [%]     | 17 ± 2    | 13 ± 1    | 8 ± 1     | 7 ± 1     |

3.3. Corrosion properties

Corrosion properties were measured in SBF for 14 days at 37 °C and the values calculated based on the weight changes are summarized in table 2. Measured corrosion rates are generally high even for pure magnesium. A high corrosion rate is associated with the presence of oxides on the boundary between the original particles [18]. Such places are prone to corrosion and the corrosion front spreads easily there. A similar finding was observed in the material prepared by spark plasma sintering [19]. In this case, the amount of oxides increased with higher extrusion temperature like the corrosion rate. The corrosion rate was also enhanced by the increased amount of Fe in the structure. Corrosion rate might be reduced after disruption of continuous oxide borders between particles for example by a higher extrusion ratio or ECAP [20]. Another possibility is to avoid the creation of oxides at all by hot vacuum pressing (HVP) which eliminates the air between particles. Nevertheless, there would be still some oxide on the surface of the powder. It could be eliminated by pre-treatment of the powder for example by HF [21].

Table 2: Corrosion rate in SBF.

|       | Ex 200 | Ex 300 | Ex 400 | Ex 500 |
|-------|--------|--------|--------|--------|
| \( v_{cor} \) [mm·a⁻¹] | 7.4 ± 1.0 | 8.2 ± 0.5 | 8.7 ± 0.6 | 9.9 ± 0.7 |
4. Conclusion
Extrusion of pure magnesium in the form of compacted tablets from atomized powder resulted in a non-uniform microstructure. Individual powder particles surrounded by oxides have been observed. Higher extrusion temperature increased the amount of oxides in the microstructure as well as the grain size. The texture was strongest in the material extruded at 500 °C, which caused great anisotropy of mechanical properties, where the difference between CYS and TYS was almost 130 MPa. Contrary, no anisotropy, and the low texture strength were measured for the extruded product at 200 °C. Microstructure with oxides surrounding each particle together with high Fe content resulted in a very high corrosion rate for all materials, which could be partly reduced by a higher extrusion ratio or by pre-treatment of the powder.

Acknowledgment
This work was supported by the grant of Specific university research – grant No. A1_FCHT_2020_003.

References
[1] Wang H, Shi Z M and Yang K 2009 Magnesium and magnesium alloys as degradable metallic biomaterials. In: 4th International Light Metals Technology Biennial Conference (LMT2009), ed M S Dargusch and S M Keay (Gold Coast, Queensland: Trans Tech Publications Inc.) pp 207-10
[2] Levorova J, Duskova J, Drahos M, Vrbova R, Vojtech D, Kubasek J, Bartos M, Dugova L, Ullmann D and Foltan R 2018 J. Biomater. Appl. 32 886-95
[3] Witte F, Hort N, Vogt C, Cohen S, Kainer K U, Willumeit R and Feyerabend F 2008 Curr. Opin. Solid State Mater. Sci. 12 63-72
[4] Kubasek J, Dvorsky D, Cavojsky M, Vojtech D, Beronska N and Fousová M 2017 J. Mater. Sci. Technol. 33 652-60
[5] Cabeza S, Garces G, Perez P and Adeva P 2015 J. Mech. Behav. Biomed. 46 115-26
[6] Yoshihito Kawamura K H, Akihisa Inoue, Tsuyoshi Masumoto 2001 Special Issue on Platform Science and Technology for Advanced Magnesium Alloys 42 1172-6
[7] Zhang X, Yuan G, Niu J, Fu P and Ding W 2012 J Mech Behav Biomed Mater 9 153-62
[8] Elsayed A, Umeda J and Kondoh K 2011 Mater. Des. 32 4590-7
[9] Kleiner S and Uggowitzer P J 2004 Mater. Sci. Eng., A 379 258-63
[10] Dvorsky D, Kubasek J, Vojtech D and Feyerabend F 2008 Curr. Opin. Solid State Mater. Sci. 12 63-72
[11] Muller L and Muller F A 2006 Acta Biomater. 2 181-9
[12] Cavojsky M, Trembosova V, Beronska N, Nagy S and Nosko M 2019 Metallic Materials 57 371-6
[13] Perez P, Garces G and Adeva P 2007 Journal of Materials Science 42 3969-76
[14] Kubasek J, Vojtech D and Dvorsky D 2017 Mater. Technol. 51 289-96
[15] Lei W, Zhu D, Wang H and Liang W 2019 Journal of Wuhan University of Technology-Mater. Sci. Ed. 34 1193-6
[16] Gu X-N and Zheng J-F 2010 Front. Mater. Sci. 4 111-5
[17] Dvorsky D, Kubasek J and Vojtech D 2020 Manufacturing Technology Journal 20 708-13
[18] Narita K, Hiromoto S, Kobayashi E and Sato T 2021 Metals 11 227
[19] Dvorsky D, Kubasek J and Vojtech D 2018 Mater. Lett. 227 78-81
[20] Minarik P, Krul P, Pesicka J, Danis S and Janecek M 2016 Mater. Charact. 112 1-10
[21] Dvorsky D, Kubasek J and Vojtech D 2019 Manuf. Technol. 19 740-4