THE STRUCTURE AND MECHANICAL PROPERTIES OF THE Zn-1.6Mg ALLOY PREPARED BY RAPID SOLIDIFICATION

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Abstract

In this work, a Zn-1.6Mg alloy was studied. The alloy composition was chosen according to the results of our previous work, which was focused on the research of biodegradable materials. The mechanical properties of such cast alloy are similar to the characteristics of human bones. Moreover, the Zn-1.6Mg alloy satisfies the requirements of biocompatibility. These facts determine the alloy for use in medicine as a suitable material for temporary implants. The alloy was studied in three different stages of processing: a cast form, an extruded form and, finally, a rapidly solidified alloy prepared by melt-spinning with the following hot extrusion. The main aim was to prepare a Zn-1.6Mg alloy with fine structure which ensures the improvement of mechanical properties. Microstructure was evaluated by optical and electron microscopy; mechanical properties (compressive strength, hardness) were measured and corrosion rate was evaluated in model physiological solution.

Keywords: Biodegradable material; zinc; magnesium

1.　　INTRODUCTION

Zn-Mg alloys have been tested as biodegradable alloys at different applications. The biodegradable materials are used as a temporary replacement of damaged tissues in the human body where the alloys gradually degrade [1, 2]. Therefore, after healing of the damaged tissue, reoperation for the removing of the implant is not required. Thus, the patient is spared of other operations and, moreover, also cost associated with the treatment is reduced. Zinc and magnesium meet the condition of biocompatibility - single metals or possible degradation products are not toxic to the body or carcinogenic and they do not cause allergic reactions. Zn and Mg are biogenic elements and they are important for the proper functionality of many vital functions in the human body. The *recommended daily allowance* (RDA) of magnesium for the human body is 300-400 mg. The human body is able to self-regulate excess amount when the daily limit is exceeded. For zinc, the *recommended daily allowance* (RDA) is lower - 15-40 mg [3]. For pure magnesium, the high corrosion rate is a problem, since it is associated with the release of large quantity of hydrogen, the increase of pH and, finally, the deterioration of the material [4]. By combining zinc and magnesium, a lower corrosion rate should be achieved. Moreover, zinc improves the mechanical properties (compressive strength and hardness) and therefore the mechanical properties compared to Mg-Zn alloys should be improved [5].

In this work, particular attention was paid to the Zn-1.6Mg alloy. This composition was selected because of its mechanical properties approaching the properties of human bone [3]. Alloys the having higher content of magnesium were found fragile and behaved as micro-galvanic a cell that was caused by different nobility of Zn and Mg. The micro-galvanic cells were formed between Zn intermetallic matrix and emerging phases and it increased corrosion rate. For alloys with lower Mg content and fine-grained structure, this effect is less pronounced [4].

The tested alloy was characterized in three different states of processing. The main objective was to prepare an alloy with the finest structure. The examined phases of processing were following: the state of cast, extruded alloy and, finally, rapidly solidified alloy prepared by melt-spinning followed by extrusion. The microstructure

was evaluated by optical and electron microscopy, mechanical properties (pressure test, Vickers hardness) were determined and, also, corrosion rate in model physiological solution was tested.

2.   EXPERIMENT

For the preparation of alloy, pure Zn (99.95 %) and pure Mg (99.9 %) were used. The Zn-1.6Mg alloy was cast into a brass mold in ambient atmosphere. The homogeneity of structure was achieved by intensive mixing by a graphite rod. The temperature of casting did not exceed 500 °C. The composition of the prepared alloy was verified by X-ray fluorescence analysis (XRF).

Then individual doses (approximately 100 g each) were prepared for the manufacture of tin ribbons. At this case, the casting temperature was 450 °C and protective Ar atmosphere was used. The molten batch was extruded by a rotating disk of copper (**Fig. 1**). Three values of rotation speed 9 m / s (10 Hz), 19 m / s (20 Hz) and 28 m / s (30 Hz) - were chosen.
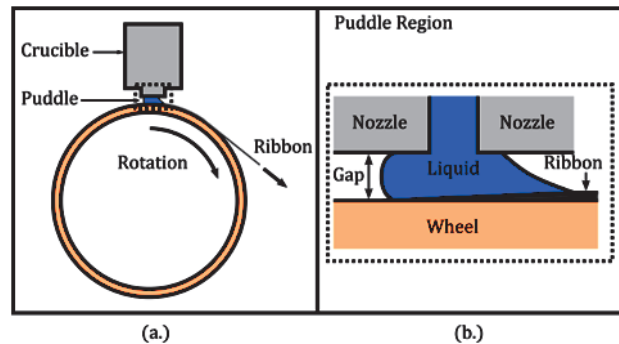

Fig. 1 The method of melt spinning a) an overall diagram, b) detail of melt contact with melt spinning wheel [6]

The ribbons were mechanically crushed and they were subsequently compacted at ambient temperature under the load of 70 KN. The prepared compact tablets were extruded at 300 °C. The ratio between the surface of samples and the constrictions (the extrusion ratio) was 10. The structure of rapidly solidified alloy was observed using a light metallographic microscope (Olympus PME-3). The details of structure were documented by scanning electron microscope with an EDS analyzer (TESCAN VEGA 3 LMU, Oxford Instruments). The phase composition was verified by X-ray diffraction analysis (XRD) using X´Pert Pro. Mechanical properties were determined by Vicker hardness measurement (HV5) and a pressure test (yield strength).

The corrosion rate of alloys was measured using an exposure test (ASTM standard G-31-72) three times for each alloy. For the corrosion test, a physiological solution of 9 g NaCl in 1 l of demineralized water was used (which is similar to blood plasma containing chloride ions). The samples (5 mm in diameter, 5 mm in height), were weighed before inserting into the solution. The exposure testing was carried out at 37 °C for 168 hours (t) in 500 ml of solution in a closed container. After the exposure tests, corrosion products were chemically removed (by aqueous solution of 200 g CrO_3 in 1 l of water at 80 °C according to ISO 8407). Subsequently, the samples were weighed. The corrosion rates (v_c) in mm per year was calculated from weight loss (Δm) according to the following **eq. (1)**:

$$v_c = (\Delta m / \rho\, S\, t)\; 8760 \quad (mm / a) \tag{1}$$

The density of Zn-1.6Mg alloy (ρ) was exactly calculated according to the alloy composition. During the exposure, the pH change of solutions was measured, as well.

The structure, mechanical properties and corrosion behavior were compared in a cast state (marked as C), after hot extrusion at 300 °C (marked as E) and, finally, with a sample rapidly solidified, pressed in a form and hot extruded (marked as RS+E).

3.   RESULTS AND DISCUSSION

A picture of thin ribbon which was prepared by the melt-spinning method is in the **Fig. 2a**. In the cross-section picture (**Fig. 2b**), there is visible microstructure inhomogeneity on one side of the ribbon. The shape and size of grains vary with the distance from the cooling wheel. The smallest grains were formed in tight contact with

the cooling wheel, where the fastest cooling was achieved. On the opposite side of the ribbon, metastable phases with the largest grains were crystalized (**Fig. 2b**). The microstructure of thin ribbon was in detail documented by scanning electron microscope (**Fig. 2c**).
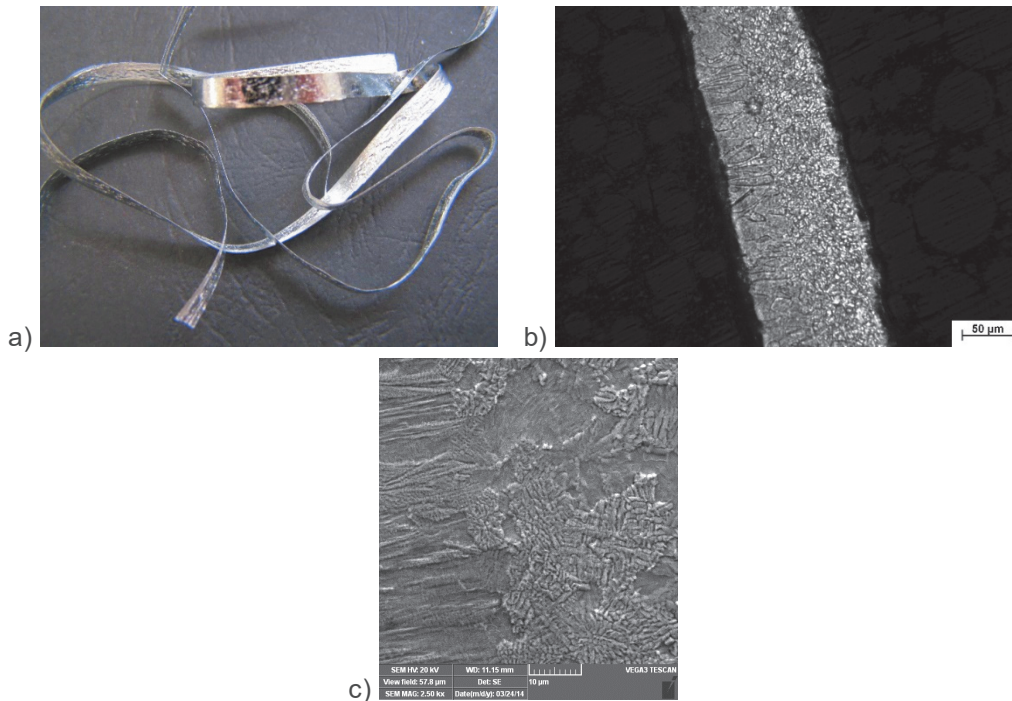

Fig. 2 a) Rapidly solidified ribbon   b) The microstructure of thin ribbon   c) Detail of ribbon
(rotation speed 10 Hz)   (cross-section)   microstructure

The comparison of the Zn-1.6Mg alloy microstructures after different treatment (as cast condition (marked as C), hot extrurusion (marked as E) and rapid solidification by melt-spinning method (marked as RS+E)) can be seen in the **Fig. 3**.

The **Fig. 3a** presents the microstructure of the Zn-1.6Mg as cast alloy. The coarse-grained structure contains primarily α-Zn phase (light areas) and α-Zn +Mg_2Zn_{11} eutectic (dark areas). The effect of the hot extrusion is documented in the **Fig. 3b**, **c**. The fine-grained structure is visible especially in the cross-section picture. The alloy prepared by the rapid solidification method (melt-spinning followed by extrusion) produced the finest microstructure (**Fig. 3d**, **e**). In the longitudinal section, the grain orientation in the direction of extrusion is clearly visible.
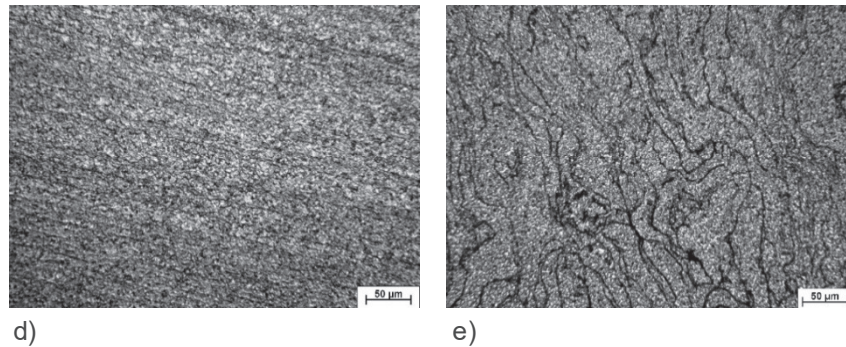
d)   e)
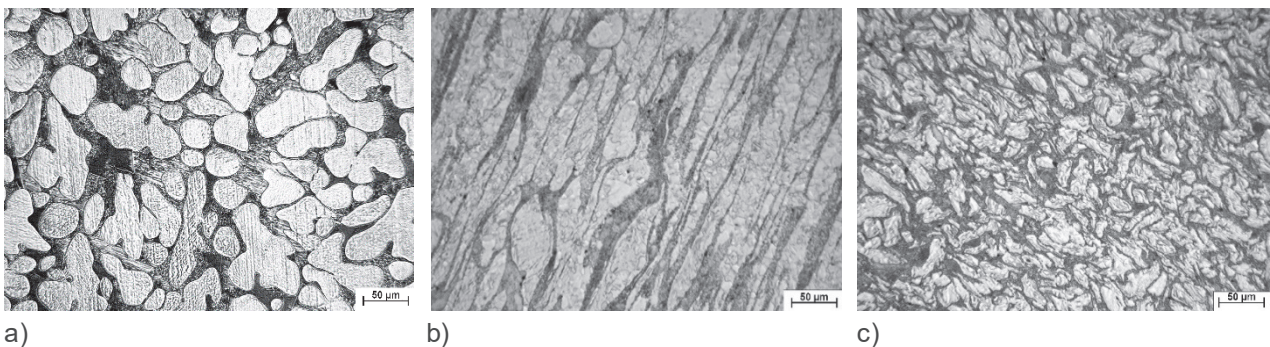
Fig. 3 The microstructure of Zn-1.6Mg (same magnification): a) as cast: primarily α-Zn phase (light areas) and α-Zn +Mg_2Zn_{11} eutectic (dark areas); b) after hot extrusion at 300 °C (longitudinal section); c) after hot extrusion at 300 °C (cross section); d) after rapid solidification at 10 Hz (longitudinal section); e) after rapid solidification at 10 Hz (cross-section). All samples were etched with a solution of 40 g CrO_3, 3 g Na_2SO_4, 200 ml H_2O
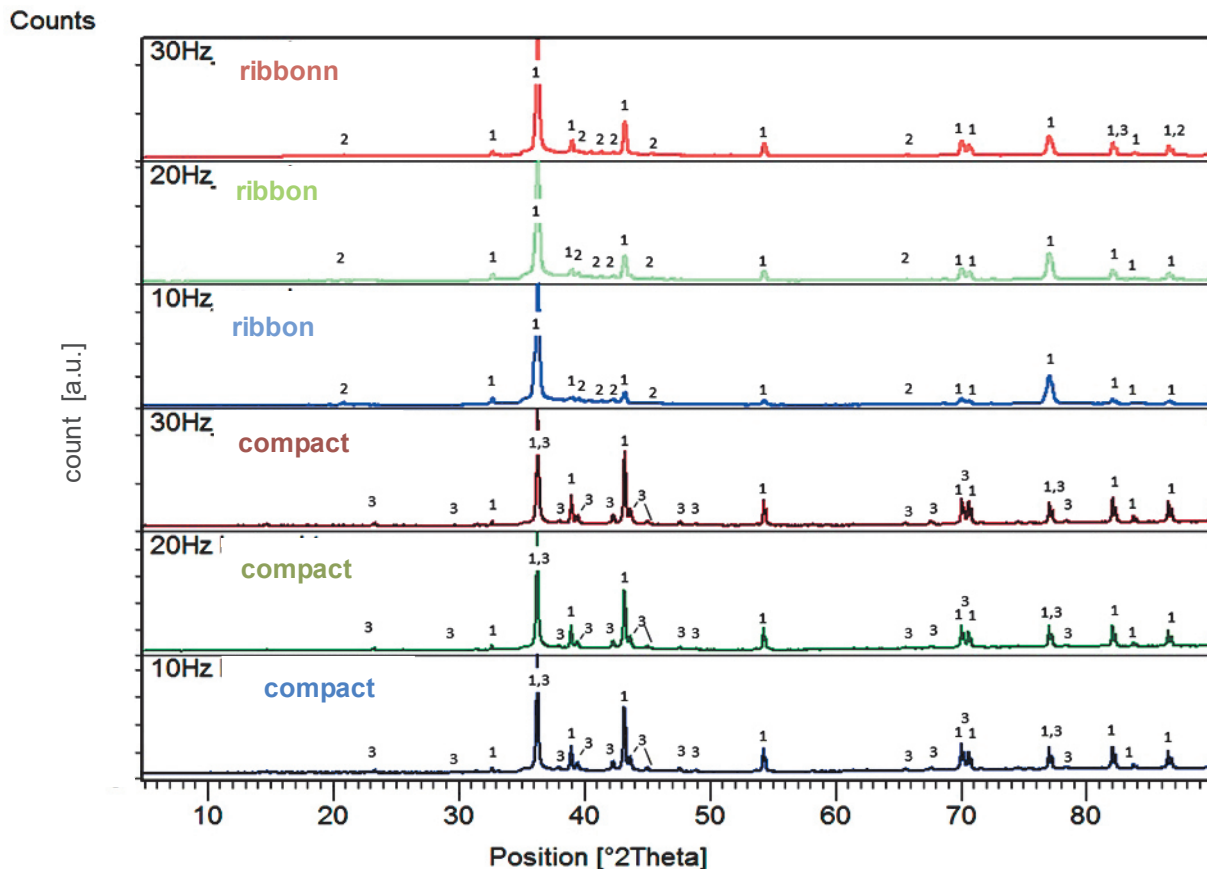

Fig. 4 XRD diffractogram of the Zn-1.6Mg alloy ribbons prepared by the melt-spinning and also of compact samples prepared by the pressing followed by the hot extrusion (α-Zn phase marked as 1; $MgZn_2$ phase marked as 2; Mg_2Zn_{11} phase marked as 3)

The phase composition of ribbons and compacts were verified by X-ray diffraction analysis (**Fig. 4**). Three speeds of rotation during the solidification of ribbons (10 Hz, 20 Hz, 30 Hz) was compared. The ratio of present phases ($MgZn_2$ and Mg_2Zn_{11}) was changed with the rotation speed only slightly. The negligible influence of the rotation speed was demonstrated also at the comparison after pressing followed by extrusion.

Table 1 Mechanical properties of prepared alloys

	Hardness	Tensile yield strength
	(HV$_5$)	(MPa)
as cast	82	315
extruded	93	385
RS+E (10 Hz)	120	423
RS+E (20 Hz)	123	424
RS+E (30 Hz)	124	348

The **Table 1** presents the mechanical properties of all prepared alloys. The hardness of the cast alloy was increased by the extrusion process. After rapid solidification, a further increase was achieved a fine-grained structure and due to the presence of Mg$_2$Zn$_{11}$ intermetallic phases. The values of tensile yield strength (TYS) are also summarized in the **Table 1**. There is a similar trend as in the hardness value measurement. Fine grain structure of the alloys prepared by the melt-spinning (with subsequent compaction and hot extrusion) noticeably improves the mechanical properties of the material. The highest rotation speed did not ensure sufficient cooling rate and therefore the value of the yield strength was lower.

The corrosion behavior of alloys was tested by corrosion exposure tests in a model physiological solution. Corrosion rates were determined from the weight loss in time. The **Fig. 5** shows that the finer structure of the material causes slower corrosion in comparison with the as cast alloys. The cooling rate during the rapid solidification had no influence on the corrosion behavior.
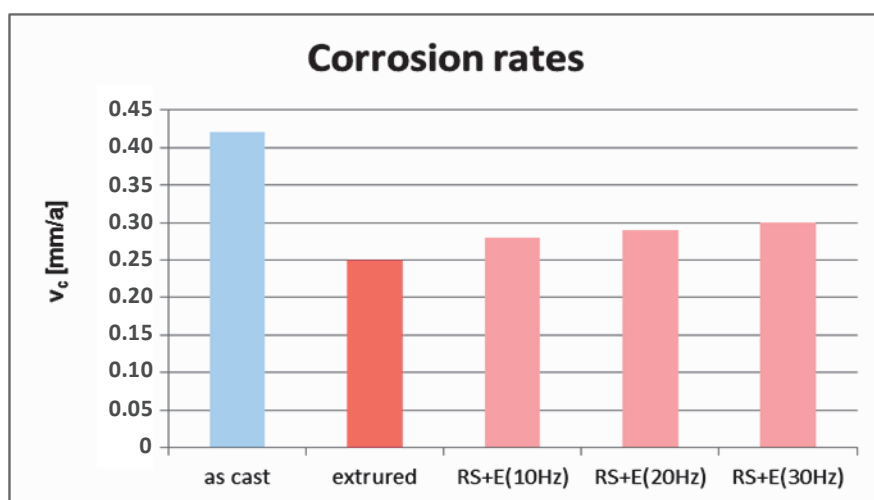

Fig. 5 Corrosion behaviors of all prepared alloys in a model physiological solution

The initial pH of solution was 5.6 and, during the test, it was increased to a value of approximately 7.6. The increase in pH was probably caused by the formation of hydroxide ions during the corrosion process of the alloy. The composition of the corrosion products was tested after exposure using X-ray diffraction analysis. It confirmed the presence of zinc oxide ZnO and zinc dichloride oktahydroxide Zn$_5$Cl$_2$(OH)$_8$.

4. CONCLUSION

The Zn-1.6Mg alloy was prepared by the melt-spinning with different speeds of cooling (10 Hz, 20 Hz, 30 Hz). The resulting thin ribbons were crushed and subsequently compacted at ambient temperature and, finally, extruded at 300 °C. This method of preparation resulted in significant improvement of microstructure. The

phase composition, mechanical properties and corrosion behavior were compared with an alloy of the same composition either as-cast or after extrusion.

The evaluation of alloy microstructure clearly showed a significant improvement after the rapid solidification.

Also mechanical properties and the corrosion rate were improved using this method.

The further aim of this work was to compare the influence of the melt-spinning cooling rates on mechanical properties (the cooling rate of 10 Hz, 20 Hz and 30 Hz were compared).

When the cooling rate 30 Hz was used the adherence between ribbon and wheel was decreased. This fact caused the coarsening of grains and the deterioration of mechanical properties comparing to the other cooling speeds. Therefore, the cooling rate of 30 Hz cannot be recommended.

The Zn-1.6Mg alloy is suitable for use as a biodegradable material and may be a good candidate for replacement for magnesium alloys. It fulfils mechanical requirements and has appropriate corrosion rate. The alkalinity around the implant and the hydrogen evolution are reduced and the healing of the surrounding tissue is promoted. In the future work, the tensile test will be further measured.

ACKNOWLEDGEMENTS

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