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Zinc Alloys as Prospective Materials for Biodegradable Medical Devices

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Zinc-based materials are considered as promising materials for an application like biodegradable medical devices (bone fixations, stents). Such materials have to be characterized by an excellent combination of mechanical, corrosion and biological properties. Presented paper is focused on the characterization of microstructure and closely related mechanical properties for 3 zinc materials, namely pure Zn, Zn-0.8Mg and Zn-0.8Mg-0.2Sr. Studied alloys were prepared by gravity casting, homogenization treatment at 350 °C and extrusion at 200 °C and extrusion ratio 11. Alloying by Mg caused the refinement of microstructure, formation of Mg_2Zn_{11} phase and related improvement of mechanical properties like TYS and UTS for an extruded alloy. An additional encore of Sr causes a systematical improvement of TYS and UTS values, although the elongation vas slightly decreased due to the presence of brittle $SrZn_{13}$ phase.

Keywords: Zinc, magnesium, biodegradable materials, mechanical properties

1 Introduction

In the last decade, the development of biodegradable zinc-based materials recorded a significant increase. Such observation is caused by several facts: 1) Zinc is an essential element for the human organism which affect various vital functions and his well acceptable daily dose for an adult is about 20 mg/day, suggesting excellent biocompatibility of this element for the human organism. 2) Zinc is generally characterized by better corrosion resistance compared to the magnesium and its alloys. Besides, the corrosion process is not accompanied by hydrogen release, which causes various complications in the case of biodegradable Mg-based materials. 3) Zinc is less prone to the impurities like in the case of Mg, where element like Fe, Cu, Ni, Co cause significant deterioration of corrosion resistance [1-5].

The mechanical properties of pure zinc are poor, therefore improvement by suitable alloying in combination with thermomechanical processing makes sense. In this case, Mg seems to be a suitable alloying element because it is characterized by excellent biocompatibility and good strengthening effect for Zn-based alloys. Specific concentration equal to 0.8 wt. % has been selected based on the previous experiences and data presented in the literature. Generally, it has been observed that the addition of Mg to Zn in the amount higher than 1 wt. % causes a significant decrease in elongation [4,6-9]. Strontium has been selected as a ternary alloying element due to its good biocompatibility and positive effect on bone resorption [2-4,10]. Since Sr tends to form with Zn brittle intermetallic phases [10] and the fact that concentrations of Mg should not be higher than 1 wt. %, we selected appropriate concentration of alloying elements (0.8 wt. % Mg and 0.2 wt. % Sr), which sum is equal to 1 wt. %.

Improvement of mechanical properties by alloying is generally insufficient and hot extrusion or hot rolling, which enable materials recrystallization and breakage of intermetallic phases are generally used [1-4]. Therefore, in presented work, the extrusion process in laboratory conditions with an extrusion temperature of 200 °C and relatively small extrusion ration equal to 11 have been selected to obtain some preliminary results about processing and concomitant behaviour of selected materials.

2 Materials and methods

2.1 Materials

Pure Zn was remelted in a graphite crucible in resistance furnace at 550 °C and cast into the brass mould with 20 mm in diameter. Zn-08Mg and Zn-0.8Mg-0.2 Sr alloys were prepared from pure metals at the same conditions. The melt was homogenized at 550 °C for 15 minutes. The as-casted materials were subsequently heat-treated at 350 °C for 24 hours on air to homogenize the microstructure with subsequent cooling to the water. The billets with 20 mm in diameter and 20 mm hight were prepared from as-casted ingots by machining and finally extruded in extrusion die using LabTest 5.250SP1-VM machine at 200 °C with the ram velocity 5 mm/min and extrusion ration equal to 11. The chemical composition of extruded materials is displayed in tab. 1.

***Tab. 1** Chemical composition of studied materials.*

Material designation	Zn [hm.%]	Mg [hm.%]	Sr [hm.%]
Zn	bulk	-	-
Zn-0.8Mg	bulk	0.76	-
Zn-0.8Mg-0.2Sr	bulk	0.80	0.17

2.2 Microstructure

The microstructure of studied materials was characterised by optical microscopy and scanning electron microscopy (SEM – Tescan VEGA3) equipped with energy dispersion spectrometry (EDS, AZtec). Firstly, samples were ground on SiC grinding papers (P80-P2500) and subsequently polished using diamond paste D2 and Eposil M suspension. The grain size was evaluated using image analysis by ImageJ software.

2.3 Mechanical properties

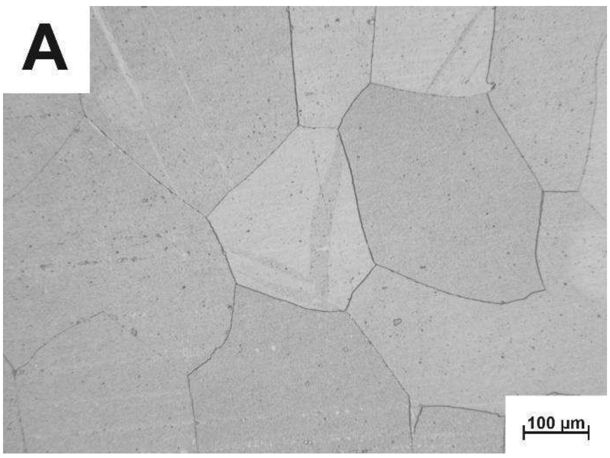
Vickers hardness measurement with loading 1 kgf and tensile tests were selected to verify the mechanical properties of studied materials. Tensile tests were performed on "dog bone" specimens with the gauge length of 20 mm and 4 mm in diameter on LabTest 5.250SP1-VM at laboratory temperature with the strain rate of 0.001 s^{-1}. Tensile yield strength (TYS) belonging to the 0.2 % proof stress, ultimate tensile strength (UTS), and elongation to fracture (A) were evaluated.

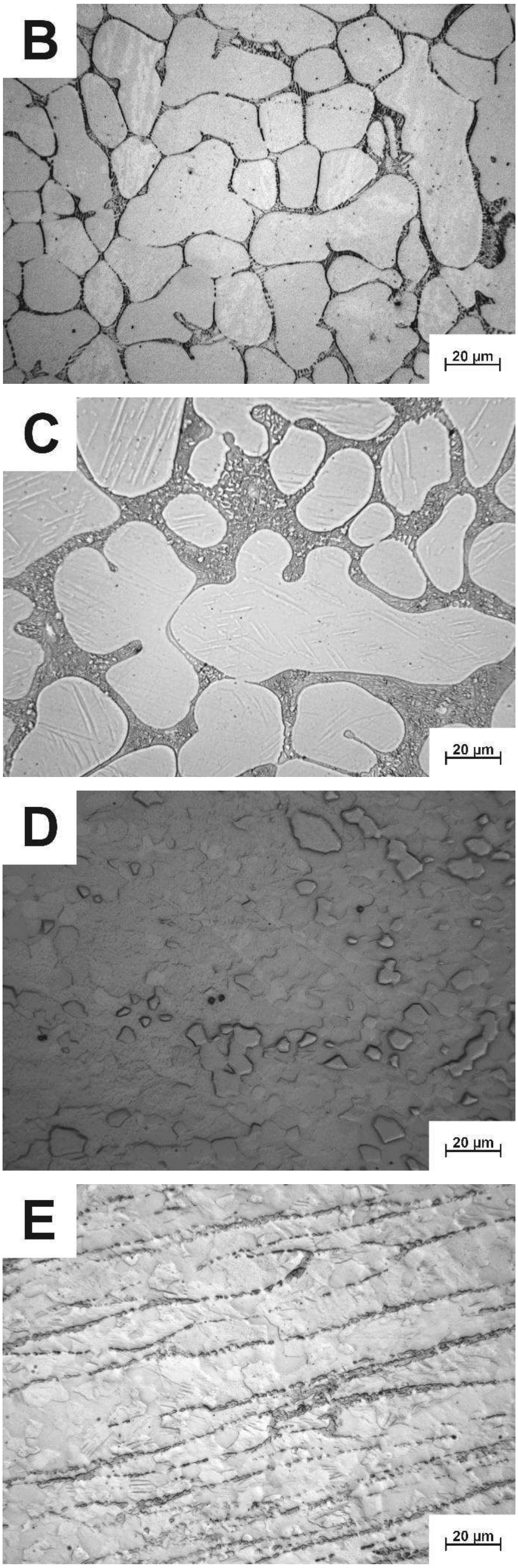
3 Results and discussion

3.1 Microstructure

The microstructure of studied materials is shown in Fig. 1. As-casted materials are characterized by relatively coarse microstructure. Pure Zn (Fig. 1A) contained large grains with 150 – 500 μm in diameter. The addition of Mg leads to the refinement of microstructure with dendrite arm spacing (DAS) about 17 μm. The similar value was observed for Zn-0.8Mg-0.2Sr alloy (Fig. 1C). During the solidification of Zn-Mg system, intermetallic phases are formed due to the almost neglectable solubility of Mg in Zn. As a consequence as-cast microstructures of both binary and ternary alloys contained a eutectic mixture of Zn and thermodynamically stable Mg_2Zn_{11} phase (Fig. 1B and 1C) occurring at the interface of dendrites. Besides, Zn-0.8Mg-0.2Sr alloy contained small particles of $SrZn_{13}$ intermetallic phase. These particles were arranged inside the eutectic mixture or at their interface with Zn matrix (Fig. 2A). The reason for such behaviour is related to the solidification of the material. Materials were melted at 550 °C, however, the solubility of Sr in Zn is neglectable at this temperature and $SrZn_{13}$ phase melts even at 830 °C [11]. After the addition of pure Sr to the melt, the solid-liquid reaction of Sr with Zn take place and solid nuclei of the resulting $SrZn_{13}$ remains in the melt till the end of solidification which is the formation of the eutectic mixture. Therefore, these phases are enclosed by the eutectic phase. Base on the XRD results (Fig. 3) binary Zn-0.8Mg alloys contained also metastable $MgZn_2$ phase. This phase is occasionally observed in as-casted Zn-Mg materials in respect to the cooling rates (12). However, such phase was not observed for Zn-08Mg-0.2Sr alloys. It is, therefore, possible, that Sr affects partially the formation of Zn-Mg intermetallic phases and support the formation of thermodynamically stable Mg_2Zn_{11} phase. Due to these differences, Zn-0.8Mg and Zn-0.8Mg-0.2 Sr alloys were heat-treated at 350 °C for 24 h before extrusion to homogenize the microstructure. It is known, that during this annealing, the eutectic phase is replaced by thermomechanically stable Mg_2Zn_{11} [12,13]. If the metastable $MgZn_2$ phase is presented in the microstructure of as-casted material, such phase is also rearranged to Mg_2Zn_{11}. Therefore, the applied thermal treatment ensures a homogeneous and clearly defined state of the microstructure before extrusion.

Extrusion process significantly affects the microstructure of processed materials. During processing, recrystallization causes significant grain refinement for all materials. Finally, pure Zn, Zn-0.8Mg and Zn-0.8Mg-0.2Sr materials are characterized by grain size 15 ± 6, 11 ± 5 and 5 ± 4 μm, respectively (Fig. 1D,E and F). For both binary and ternary extruded alloys, intermetallic phases are arranged in rows parallel to the extrusion direction (Fig. 1E and F). These phases correspond to the Mg_2Zn_{11}. Besides $SrZn_{13}$ phase remained enclosed in Mg_2Zn_{11} or at their interface with Zn matrix (Fig. 2B). The presented phase composition was documented by EDS analysis and confirmed by XRD measurements (Fig. 3). Its worth to mention that Zn-based alloys are generally characterized by specific basal texture with basal planes oriented parallel to the extrusion direction [2,4,13]. Although this behaviour was not the subject of the presented research, it is well predictable that such preferred crystallographic orientation will occur in these materials as well.





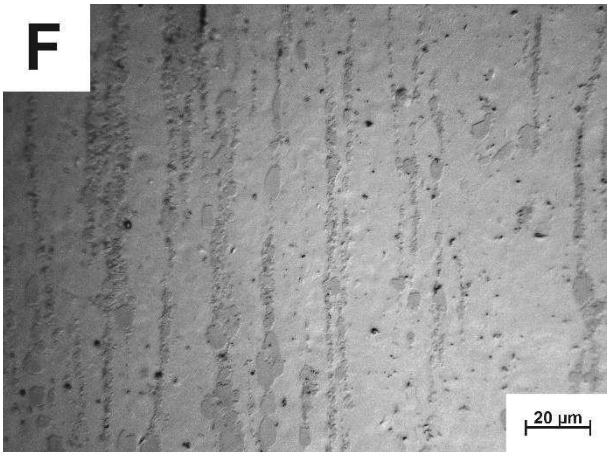


Fig. 1 *The microstructure (OM) of: A) as-cast Zn, B) as-cast Zn-0.8Mg, C) as-cast Zn-0.8Mg-0.2Sr, D) as-extruded Zn, E) as-extruded Zn-0.8Mg, F) as-extruded Zn-0.8Mg-0.2Sr.*

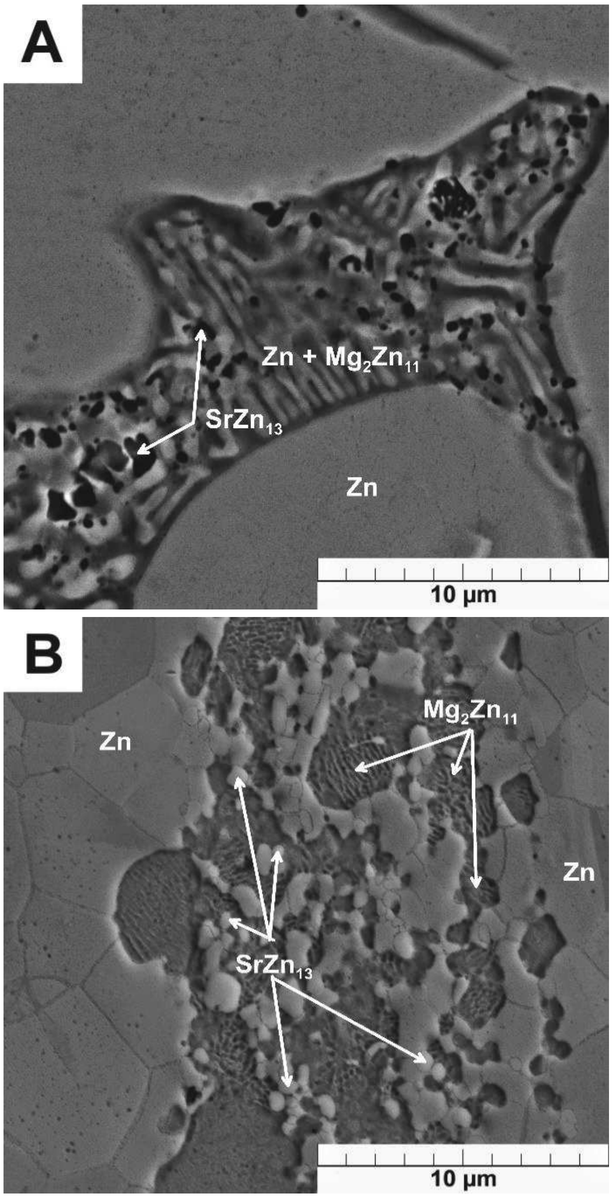


Fig. 2 *The microstructure (SEM) of: A) as-cast Zn-0.8Mg-0.2Sr, B) as-extruded Zn-0.8Mg-0.2Sr*

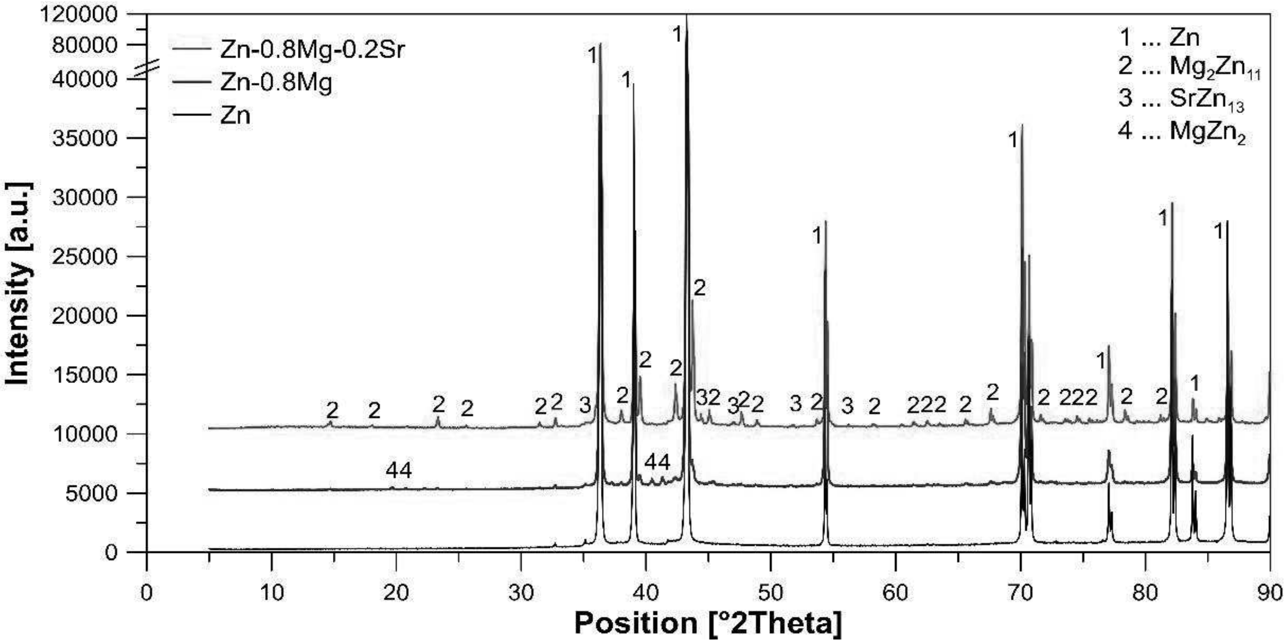


Fig. 3 *XRD patterns of extruded materials*

3.2 Mechanical properties

It is well-known that mechanical properties of the as-cast zinc alloys are characterized by poor mechanical properties, which does not fulfil general requirements for medical devices like traumatological and orthopaedical biodegradable implants. Due to neglectable solubility of Mg and Sr in Zn matrix [11], the improvement of mechanical properties by thermal treatment including artificial ageing is not possible. Therefore, various thermomechanical treatments are generally performed with the greatest use for hot extrusion or rolling. In the presented work, all materials were processed by extrusion at medium temperature 200 °C. Pure Zn is able to recrystallize at laboratory temperature [4]. Although the recrystallization temperature of alloys may be slightly higher, the selected temperature 200 °C is sufficiently high for complete recrystallization of studied materials. Significant grain refinement in combination with rearrangement of intermetallic phases to the rows parallel to the extrusion temperature causes significant improvement of mechanical properties as evident in Fig. 3 and Tab. 2. Its worth to mention that tensile properties of extruded Zn are still very poor with TYS value as low as 43 MPa. However the addition of 0.8 wt. % of Mg in combination with extrusion processing lead to the much more promising values of 203 MPa, 290 MPa and 13 % for TYS, UTS and elongation, respectively. Additional improvement has been observed for ternary Zn-0.8Mg-0.2Sr alloys indicating some positive effect of Sr addition on values of TYS and UTS. The difference between Zn-0.8Mg and Zn-0.8Mg-0.2Sr materials performance is partially attributed to the decrease in the grain size for ternary alloy and the presence of $SrZn_{13}$ intermetallic phase. Although, it is also evident that brittle $SrZn_{13}$ cause the gentle decrease of material elongation compared to the binary Zn-0.8Mg alloy. Zn-Mg and Zn-Mg-Sr alloys were studied several times [4,6-10,14]. Although presented results suggest that both alloys are characterized by acceptable tensile mechanical properties especially owing to mechanical properties observed for Mg-based alloys [15-16], TYS, UTS and A values may be still improved by modification of the extrusion process. For example, Capek et.al [13] showed that higher extrusion ratios and lower extrusion temperatures lead to the significant improvement of material elongation. Therefore, modification of these parameters for extruded Zn-0.8Mg-0.2Sr alloys worth for investigation to process material with a superior combination of strength and plasticity.

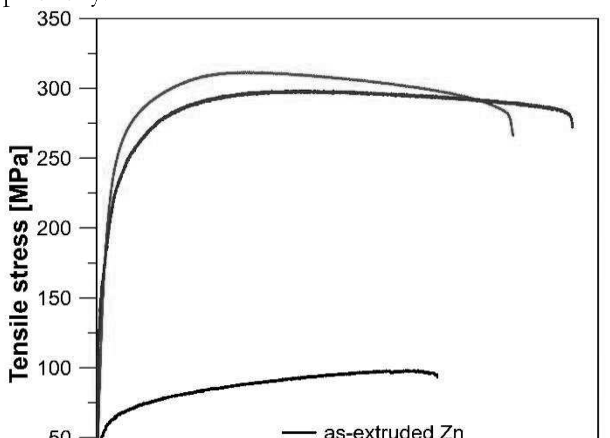


Fig. 3 *Samples of tensile stress-strain curves for Zn, Zn-0.8Mg and Zn-0.8Mg-0.2Sr in extruded conditions.*

Tab. 2 *Mechanical properties of extruded materials*

	TYS [MPa]	UTS [MPa]	A [%]	HV1
Zn	43 ± 2	89 ± 4	7.8 ± 0.5	41 ± 3
Zn-0.8Mg	203 ± 9	290 ± 11	13.2 ± 1.4	82 ± 4
Zn-0.8Mg-0.2Sr	243 ± 7	315 ± 10	10.1 ± 1.1	86 ± 3

4 Conclusion

Presented paper deals with the study of free Zn-based materials, namely Zn, Zn-0.8Mg and Zn-0.8Mg-0.2Sr. Obtained results indicated that as-cast materials are characterized by coarse-grained structures which is commonly exhibited by worse mechanical properties. Therefore, extrusion has been performed to improve material properties. The microstructure of all extruded materials was characterized by relatively fine recrystallized grains which equivalent diameter (5-15 μm) decreased in the order Zn > Zn-0.8Mg > Zn-0.8Mg-0.2Zn. Besides, both alloys contained intermetallic Mg_2Zn_{11} phase accompanied by $SrZn_{13}$ in ternary Zn-0.8Mg-0.2Sr. Such microstructure development directly affected the mechanical properties of studied materials. Both extruded alloys were characterized by significantly improved mechanical properties like TYS and UTS compared to the extruded Zn. Addition of Sr has a supplementary positive effect on the increasing value of TYS and UTS compared to the binary Zn-0.8Mg, although due to the brittleness of $SrZn_{13}$ phase, elongation to fracture is slightly decreased for the ternary alloy. Both Zn-0.8Mg and Zn-0.8Mg-0.2Sr fulfil the general requirements (TYS > 200 MPa, UTS ≈ 300 MPa) for applications like traumatological and orthopaedic implants.

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