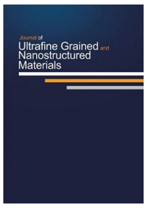

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Zinc based bioalloys processed by severe plastic deformation – A review

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ABSTRACT

Zinc based alloys have recently attracted great attention as promising biodegradable metals. Zinc exhibits moderate degradation rates in biological fluid and the zinc releases during the degradation process is considered safe to human systems. However, these materials exhibit critical limitations in terms of mechanical properties for medical applications. Adding alloying elements as well as grain refinement by thermomechanical processing are considered as effective techniques to address this problem. Severe plastic deformation (SPD) methods were considered in recent few years to process the zinc-based bioalloys to achieve acceptable mechanical characteristic while retaining their desired biocorrosion behavior. Summarizing present literature implied that Mg, Ag, Mn, and Ca containing zinc bioalloys may provide an improved strength and ductility approaching the common mechanical criteria. However, due to low melting temperature of zinc, there remains new uncertainties in mechanical response as future challenge, including low creep resistance and high susceptibility to natural aging at body temperature.

Keywords: *Zinc alloys; Severe plastic deformation; Microstructure; Mechanical properties*

Introduction

The development of metallic biomaterials is one of the trending fields in material science to improving human life. A biodegradable metals as new generation can overcome many of the side effects of permanent ones [1]. Previous reports indicate that magnesium and iron biodegradable based metals have been extensively studied despite its excellent biocompatibility, limited success has been achieved due to their poor degradation behavior [2]. The degradation rate of Mg-based alloys was too high and released a significant amount of hydrogen, which may cause the rapid loss of mechanical integrity [3]. In contrast, Fe- based alloys showed too slow corrosion rate and voluminous iron oxide products [4,5].

Since 2013, increasing attention has been focused on Zn and its alloys as a class of biodegradable materials due to their biocompatibility. Zn plays important roles in many biological process in human body, owing to their nontoxicity and biodegradability. Zinc with standard electrode potential of -0.8V, which is between that of Mg and Fe, offer an appropriate corrosion rate. Moreover, it may be processed through easy manufacturing due to relatively low melting point and low reactivity in molten state [6,7]. However, pure zinc has inadequate mechanical properties (low yield stress of ~20MPa and ductility of ~12% [8]) and suffer from low creep resistance, high susceptibility to natural aging, and static recrystallization (SRX). Due to the mechanical properties limitations, Zn could not satisfy the clinical requirements for medical applications.

In recent years, two strategies have been employed to improve the mechanical performance of pure zinc, including alloying with other elements and thermo-mechanical treatments. A remarkable increase in strength and ductility could be attained in Zn-based materials through alloying addition such as Mg and Mn [11]. However, grain refinement through TMP processes is considered as more effective promising way in this regards. Modification on thermo mechanical treatment enables obtaining fine grained microstructures as well as optimizing other strengthening mechanisms such as precipitation hardening [12]. Outstanding refining of grain size requires, application of extreme value of plastic deformation on material[13]. Accordingly, a possible avenue for microstructure refinement of metals is severe plastic deformation (SPD), which has been widely used to fabricate ultrafine/nano grained metals and alloys through introducing a large plastic strain into a bulk metal. A variety of SPD methods, such as equal channel angular pressing (ECAP), accumulative roll bonding (ARB), twist extrusion, accumulative back extrusion have been proved to be feasible to produce sub-micrometer or nanometer sized grains in different metals and alloys, e.g. [14-17].

However, quite rare researches could be found in literature dealing with the SPD processing of Zinc alloys. In this work, the SPD trails on Zinc based alloys were reviewed with the focus on the alloys designed and developed for biomedical application. The obtained microstructure, mechanical and corrosion properties were summarized.

1. Alloy systems

One of the most powerful tools to overcome performance limitation of Zinc is the addition of alloying elements to the pure metal matrix. Nevertheless, the biocompatibility of absorbable biomaterial components must be considered, given that all elements of the metal alloy will eventually pass through the human body [18]. To date a few researches had dealt with modifying chemical composition of zinc alloys. The principal alloying elements are briefly discussed below.

Studies of Zinc alloys as a biomaterials, were started from 2011 by Vojtěch [8] who worked on the structure, mechanical properties and corrosion behavior of Zn-Mg alloys containing up to 3 wt% Mg. Magnesium is considered as the most well know biocompatible and biodegradable element [19]. According to very limited solubility of Mg element in Zinc, it may easily constitute intermetallic particles during casting, which render the Zn-Mg alloys as age-hardenable materials.

Aluminum is the most commonly used alloying element in current Zn alloys available on the market. Zn-Al alloys are also the most documented Zn alloys in literature and they are designed for inexpensive structural and decorative parts in automotive, electronics and household sectors. Aluminum is recognized as a neurotoxin which causes cognitive deficiency. However, Bowen et al. [20] pointed out that, considering a potential Zn-Al alloy stent, the absorbed daily dose of Al would be far below the recommended value for humans.

Copper is a nutrition element for human health, which serve as an essential precursor for development of connective tissues, nerve coverings and bone growth [21]. Therefore, trace Cu addition in Zn-based alloys would be of great advantages. Copper has a moderate solubility in Zn (2.75 wt.% Cu in Zn at 425°C). As-cast Zn-Cu alloys are composed of two-phase, primary ε- $CuZn_5$ dendrites and η-Zn solid solution. Tang et al [22] conducted research on Zn-xCu (x=1, 2, 3, and 4 wt%) alloys. They revealed that as Cu content increases more Cu Zn_5 phase precipitates.

Manganese (Mn) is an essential trace element with acceptable blood compatibility which can be added in biodegradable Zinc based alloys [23] . On the other hand, Mn by removing the heavy metal elements has much effect on corrosion properties. Mn has low solubility in Zn (~ 0.8 wt % in Zn at 405°C). In as-cast Zn–(<1 wt%)Mn alloys, $MnZn_{13}$ phase mainly locates at grain boundaries as a structural component of Zn/$MnZn_{13}$ Mneutectic structure [11].

Lithium is reported to be beneficial in several treatments such as brain injury, stroke, Alzheimer's, Huntington's and Parkinson's diseases and spinal cord injury, provided that it is kept below a critical content. Based on clinical experiences, Li is nontoxic in the therapeutic range of 0.6–1.0 mM, while the toxic level occurs at 1.4 mM or higher [10]. Li has a relatively low solubility in Zn (about 0.12 wt. % at 403°C) and therefore, under an equilibrium cooling condition, for any Li content above 0.12 wt% (within the eutectic range), Li has a tendency to form a lamellar Zn+$LiZn_4$ eutectic micro-constituent along the α-Zn grain boundaries [24]. Zn-Li alloy showed good mechanical properties and biocompatibility. The results for the Zn-Li alloy at 11 months in vivo indicated good biocompatibility.

Calcium and Sr are well-known essential nutrient elements, constituting major components of bone tissue [25]. Ca is the most abundant mineral element in human body, which is therefore naturally selected as an alloying element of pure Zn and its alloys in order to adjust their properties. Ca addition can modify mechanical properties and biocompatibility of pure Zn. Sr is known as an osteopromotive element which can activate osteoblastic cell replication and decrease bone resorption while stimulating bone formation. Calcium and Sr have no solubility in Zn and even in dilute Zn alloy systems they react with Zn, leading to the formation of $CaZn_{13}$ and $SrZn_{13}$ intermetallic compounds [6] . Ca and Sr are attractive alloying elements for an orthopedic biodegradable implant material.

2. Microstructural Evolutions

The main microstructure features which are influenced by SPD processing include the grain size distribution, dislocation substructure and second phase particles. In case of biomedical zinc alloys, limited works could be found in the literature with a detailed discussion on microstructure evolution. The main researches are summarized in Table 1 and reviewed in the following.

2.1. Grain refinement

Deformation of zinc alloy is governed by a variety deformation mode including basal, pyramidal and twinning systems [33]. At the absence of enough slip systems, twinning is found to occur [34]. Accordingly, basal slip operates at the lowest stress, but contributes only two independent slip systems. To achieve a homogenous deformation, according to Taylor criteria, either pyramidal slip or twinning must operate in addition to basal slip. Pyramidal slip is thermally activated, and is therefore favored at high temperatures. Thus, SPD processing of

Table 1- Mechanical properties of Zinc based alloy processed by SPD

Composition	Strain rate	Average grain size (μm)	Elongation (%)	Yield stress (MPa)	Tensile strength (MPa)	Year	ref
Zn-3Mg (1-ECAP,200 °C)	0.5 mm/min	2.3	4.6	137	153	2017	[26]
Zn-3Mg (2-ECAP,200 °C)	0.5 mm/min	1.8	6.3	205	202	2017	[26]
Zn-0.5Cu ECAP at RT	$1\ s^{-1}$	1	19	210	310	2018	[27]
Zn-0.02Mg (Extrusion at 200°C + Cold Drawing)	$1\ s^{-1}$	1	5.4	388	455	2018	[28]
Zn-0.5Mn (multi-pass hot extrusion)	$0.0001\ s^{-1}$	0.35	236.2	-	-	2019	[29]
Zn-1.6 Mg (4 p-ECAP,150°C)	$1.1\times 10^{-3}\ s^{-1}$	-	6.2	300	390	2019	[30]
Zn-1.6 Mg (12 p-ECAP,150°C)	$1.1\times 10^{-3}\ s^{-1}$	-	5.2	361	423	2019	[30]
Zn-1.6 Mg (12 p-ECAP,250°C)	$1.1\times 10^{-3}\ s^{-1}$	-	5	347	414	2019	[30]
Zn-0.42Mn ECAP at RT	$1\times 10^{-3}\ s^{-1}$	1.1	93	148	188	2019	[31]
Zn-0.82Ag ECAP at RT	$1\times 10^{-3}\ s^{-1}$	3.2	143	76	96	2019	[31]
Zn-0.49Cu ECAP at RT	$1\times 10^{-3}\ s^{-1}$	2.2	345	94	48	2019	[31]
Zn-4Ag (Extrusion + Cold Drawing)	$3.3\times 10^{-3}\ s^{-1}$	2.3	430	45	59	2020	[32]

Zn based material should be performed at high temperatures. The microstructure of Zn alloys preferably undergoes dynamic recrystallization (DRX) rather than dynamic recovery (DRV) during deformation at high temperatures [33]. This is connected with the limited active slip systems in their crystal structure. On the other hand, the SPD processing of zinc alloy at high temperatures may be accompanied with an undesired growth of DRXed grains, therefore mitigating the efficiency of grain refinement. Thus, to achieve an advantageous grain-refined microstructure the SPD conditions should be compromised.

Guo et al [29] investigated the grain size of Zn-0.5Mn alloy prepared by multi pass hot extrusion at 230 °C, where a recrystallized grains of 0.35 µm mean size were developed. With increasing deformation ratio, the higher density of subgrains were formed in the coarse grains. Bednarczyk et al [27] founded the average grain size of Zn-0.5Cu processed by multi pass ECAP at room temperature decreased from 350 µm to 1 µm due to continuous dynamic recrystallization. Their very recent study [35] showed high pressure torsion (HPT) processing of the same material develops subgrains with mean size of 1.9 µm after 10 turns. They demonstrated that twinning occurs during the initial straining and the continuous shearing cause a high density of dislocations leading to dynamic recrystallization (DRX) of coarse grains. The same research group studied that the microstructure of Zn-0.82Ag after 4 ECAP passes at room temperature [31]. A drop in mean grain size from 50 µm to 3.2 µm was observed, where the contribution of twin bands during microstructure evolution was highlighted. The occurrence of twinning at low temperature was also reported by Liu et. al. [30] in Zn-1.6Mg during ECAP at different temperatures. The literature in this area lacks systematic results on the microstructure and deformation mechanisms, leading to formation of new grains. Further studies are also necessary to recognize the effective role of twinning as well as dislocation substructure in Zn alloys during SPD experiments.

The final manufacturing process of medical devices such as stents includes cold forming methods, during which Zn alloys can undergo recrystallization due to low melting temperature of Zinc alloys [36]. Thus, the microstructure, mechanical properties and corrosion behavior may further be influenced thereof. Wang et al [28] studied the microstructure evolution of Zn-0.02Mg prepared by multi-pass drawing experiments for the first time. As depicted in Fig.1 they demonstrated that when cumulative area reduction was larger than 45%, equiaxed grains with mean size of 1µm

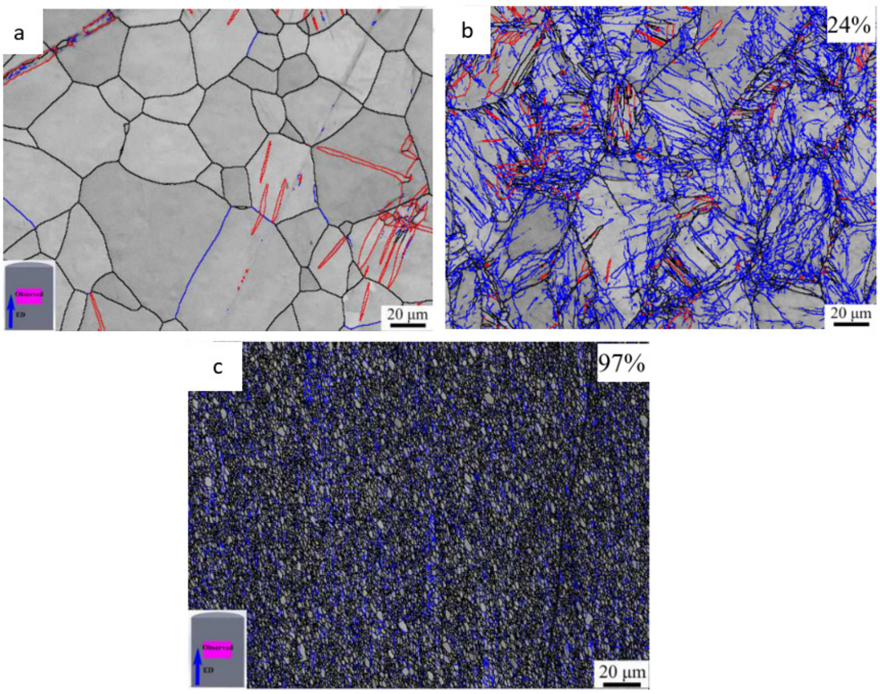

Fig. 1- Evolution of microstructure of extruded Zn-0.02Mg with different cumulative AR during drawing process (a) 0% ; (b) 24% ; (c) 97% (In the boundary misorientation maps, blue lines for LAGB (2°~15°); black lines for HAGB (>15°); red lines for {10$\bar{1}$2} twin boundaries) [28].

were formed, implying the occurrence of DRX during room temperature deformation.

2.2. Precipitation hardening

2.2.1. Particle stimulated nucleation (PSN)

Precipitation hardening was identified as the main strengthening mechanism in the SPD-processed Zn alloys containing Mg addition. Liu et al [30] revealed that nanometer-sized MgZn particles are dynamically precipitated in the matrix during multi-pass ECAP of Zn-1.6Mg alloy. The obtained particles are typically shown in Fig. 2. It was discussed that multiplication of dislocation at the grain boundaries provides easy diffusion paths for Mg atoms. According to the limited solid solubility of Mg in Zn matrix dynamic precipitation of Mg-Zn was triggered after consequent ECAP passes. Their coherent interface with the matrix and thus low precipitation energy barrier promote the formation of particles.

TEM observation (Fig.3-b) showed that the eutectic structure including $Zn+Mg_2Zn_{11}+MgZn_2$ phases may also be constituted during ECAP passes. The composition of eutectic phase is different from that in conventional Zn-Mg alloys (Fig.3-a) [30]. The results showed that thermally stable $MgZn_2$ precipitates could promote the occurrence of DRX through the (PSN) mechanism.

Ardakani et al [38] investigated the evolution of second phase particles in Zn-0.05Mg processed by cold rolling. They claimed the formation of room temperature nano-sized Mg_2Zn_{11} occur in ultra-fine grain alloys. By addition of Mn and Cu, Mg atom, diffusion rate decelerated by the presence of solution atoms, indeed kept Mg atoms in the solid solution.

Mostaed et al [32] studied Zn-4Ag-xMn(x=0, 0.2, 0.4) alloys extruded at 310°C with an extrusion

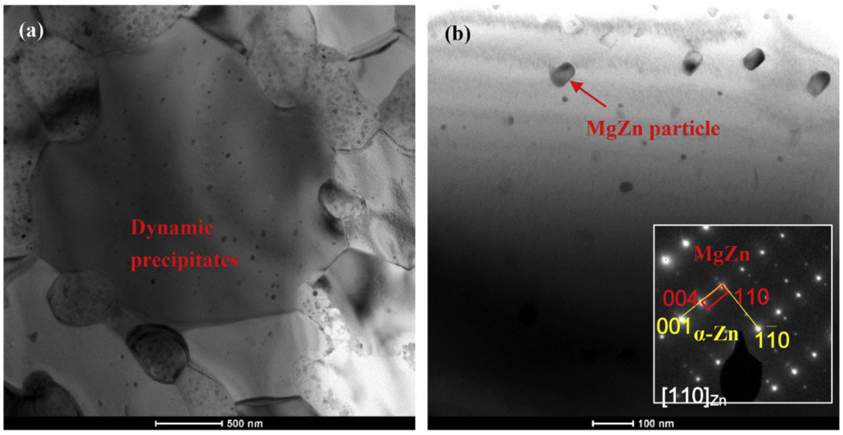

Fig. 2- TEM images of the dynamically precipitated phases in Zn grains with (a) low and (b) high magnifications, and the corresponding SAED patterns inset of (b) [30].

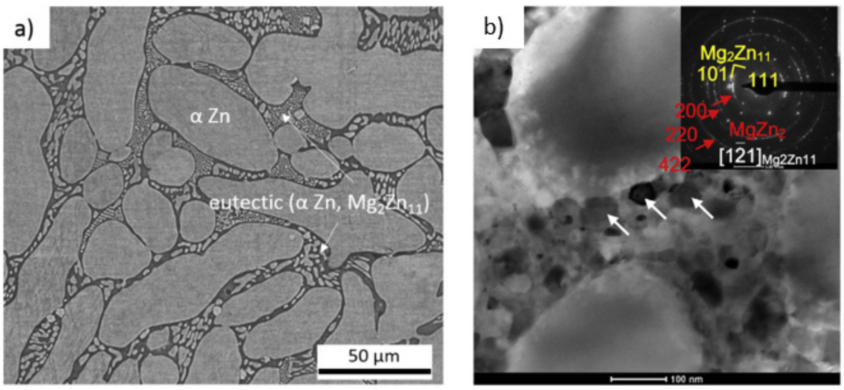

Fig. 3- (a) SEM BSE microstructures of ZnMg [37], (b) TEM images of the eutectic structure in as-cast Zn-1.6Mg alloy [30].

ratio of 39:1 with subsequent multi pass drawing at room temperature. They demonstrated that Mn-rich particles formed at the grain boundaries, where with increasing the Mn content the degree of grain refinement was promoted through PSN mechanism.

2.2.2. Pinning effect

Published researches on Zn-Mn alloys implied that second phase particles may play alternative role during SPD processing by inhibiting grain growth. Guo et al [29] showed that during multi pass hot extrusion of Zn-0.5Mn, finer formed on low angle grain boundaries, may effectively hinder the growth of subgrains. The pinning force as a function of dispersion of particles per unit area of grain boundary is estimated by the following [39]:

$$P_f = \frac{3f\gamma}{r} \tag{1}$$

where r is the size of the second phase, γ is the grain boundary surface tension per unit area, and f is the volume fraction of the second phase.

Dambatta et al [26] reported that the grain size of Zn-3Mg was decreased from about 48μm (as-cast) to 1.8μm (2-ECAP). The coarse intermetallic phase of Mn_2Zn_{11} crushed into finer $MnZn_{13}$ particles and homogenously distributes during 2-ECAP process at 210^{0}C. The pinning effect of the particle could restrict the growth of DRXed grains at the high deformation temperature.

3. Mechanical properties

Developing high strength and ductility zinc alloy with sufficient hardness, while retaining its biocompatibility, is one of the main goals of metallurgical engineering. The strength and ductility of the common zinc alloys are not sufficient according to criteria for biodegradable devices. For example it has been reported an ideal biodegradable stent should exibit tensile strength and fracture elongation exceeding 300 MPa and 25% respectively and maintain mechanical integrity for 3-6 months [6]. SPD processed Zinc alloys exhibit a wide range of ultimate tensile strengths and elongations, from 48 to 423 MPa and from 4.6% to ~345%, respectively. The final mechanical properties data were given in Table 1. It can be realized that SPD process could effectively contribute to strength and ductility of the Zn-based alloys. Moreover, SPD processed alloys present superior ductility compared the materials produced through conventional thermomechanical treatments. The degree to which SPD process improve the mechanical characteristic is dependent on the strengthening mechanisms that principally operate in the material.

The results reported by Dambatta et al [26] on Zn-3Mg alloy after two pass ECAP revealed that both strength and ductility increased from 84MPa and 1.3% to 220MPa and 6.3% respectively based on tensile curve (Fig. 4). They explained the strength of the processed material relying on the grain refining effect, while the ductility improvement was justified based on the Mg_2Zn_{11} intermetallic phase which were crushed and distributed homogenously. Huang et al [40] obtained the highest ultimate tensile strength ever reported for SPD processed zinc bio alloys. They achieve the outstanding result after eight ECAP passes of Zn-1.6Mg alloy.

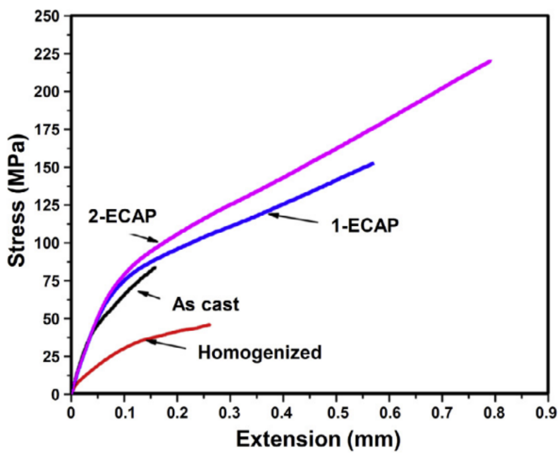

Fig. 4- Tensile curves of processed Zn-3Mg alloy reported by [26].

A superplasticity behavior was recorded for a Zn-0.5Cu alloy after 4 ECAP passes at room temperature (Fig. 5) [27]. This result was rationalized based on an increased strain rate sensitivity after exceptional grain refining. They declared that room temperature superplasticity (RTS) was due to the significant contribution of grain boundary sliding (GBS). However, Mostaed et al's findings reveal that RTS is due to a phenomenon named "precipitation softening", occurring in UFG microstructures. They assumed that the remarkably fine precipitates provide extensive amount of interfaces to take part in phase boundary sliding (PBS). Indeed, RTS is mainly dominated by PBS rather than by GBS [38].

The effect of chemical composition on the final mechanical properties of Zn bioalloy was studied by Bednarczyk et al [31], alloying with Ag, Cu and Mn. They discussed that the capability of the alloying element to activate non-basal slip system can assist in improving the mechanical properties. The latter effect is realized as decreasing the ratio $CRSS_{(non-basal)}/CRSS_{(basal)}$, where CRSS is critical resolved shear stress. Moreover, Mostaed et al [32] observed a surprising precipitation softening behavior in a Zn-4Ag alloy which result in to a final ductility of 430%.

Sun et al [41] demonstrated that ultimate yield strength of extruded Zn-X Mn (X = 0, 0.2, 0.4, 0.6 wt%) decreased from 220 MPa to 182 MPa while the fracture elongation considerably improved, from 48% to 71%. They pointed out the importance of strengthening effect of twinning in the processed material. Twining acts as barriers to the movement of dislocations so it had a key role in the mechanical properties of Zn-Mn alloys.

4. Biocorrosion properties

Good corrosion resistance was necessary to ensure excellent biocompatibility [2]. Due to interaction between corrosion products and human cells, biocompatibility is one the main considerations in selecting the implant materials. Additionally, maintaining the mechanical integrity when the medical device degrades, plays a key role in order to inhibiting the following effects such as stress shielding. Under this circumstances, optimizing the corrosion rate can be considered as a controlling tool to preventing some possible dangers. In the case of magnesium alloy, previous researches demonstrated that despite all the benefits of Mg and its alloys, a solution to reduce the rapid degradation rate as a limitation of their practical applications have not yet arrived [5]. Early interest towards Zn initiated after the published work on Mg–Zn–Ca bulk metallic glasses (with about 50 wt. % of Zn) where a significant reduction in hydrogen gas evolution during in vitro degradation was realized [42]. High purity Zn degrades at a rate of tens of micrometers per year while the natural degradation rate of pure Mg extends to the hundreds of micrometers per year [5]. The lower corrosion rate of Zn presents several advantages such as better biocompatibility.

For the first time, Bowen et al [43] exhibited that the critical aspects of biocorrosion of Zinc alloys satisfy the requirements for medical application. Accordingly, thin layer of zinc oxide and zinc carbonate were the only product observed during early stages (3 months) on the surface of zinc wires implanted in to rat aorta.

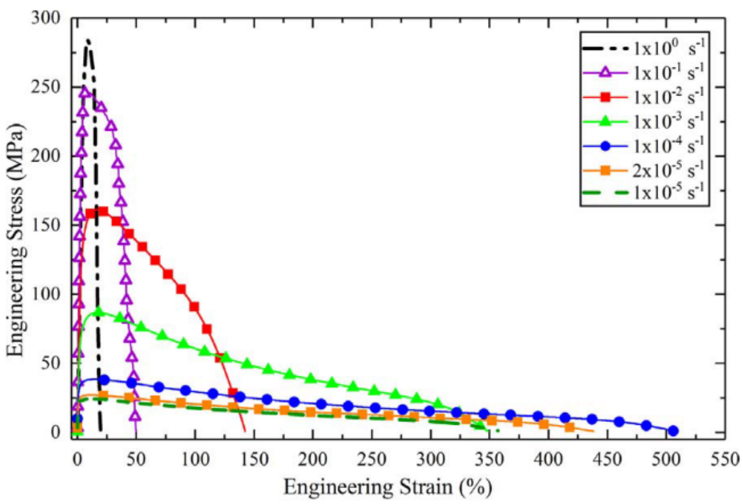

Fig. 5- Strain-stress curves of $Zn_{0.5}Cu$ alloy processed by ECAP [27].

Corrosion in polycrystalline materials is affected by grain size, however there are contradictory published data about the relationship between the grain size and the corrosion resistance, claiming that depending upon the ability of the environment to passivate, materials could experience an increase or decrease in corrosion resistance with grain refinement [44]. If corrosion progresses by active anodic dissolution, grain boundaries will accelerate the corrosion rate. Dambatta et al [26] claimed uniform distribution of intermetallic phases after ECAP processing cause lower corrosion rate of corrosion decreasing from 0.25mm/year to 0.18mm/year but on the other hand, with increasing the number of passes, Zn-3Mg samples corrode faster (0.19mm/year) due to mass transport in solid phase such as diffusion of ions through oxide layers. Indeed, grain boundary is well known as a place where impurities and solutes are dissolved. Some impurities and solutes act as effective cathodes, and accelerate the corrosion rate significantly.

Huang et al [40] indicated that Zn-1.6Mg ECAPed samples have not obvious difference in passivation behavior of the film surface with the as-cast one while the corrosion rate of ECAPed alloy showed a very small increase. However, they claimed that the SPD process could significantly improves the mechanical properties despite maintaining corrosion resistance. The corrosion behavior of a binary Zn-4.0Ag and ternary Zn-4.0Ag-xMn (where x=0.2-0.6 wt%) alloys after severe extrusion at 310 °C and then wire drawn at room temperature were investigated by Mostaed et al [32] . They showed that cold drawing alloys exhibited ultrafine-grained structure along with a dynamic precipitation of nanosized $AgZn_3$ particles. An immersion test showed that the accelerated corrosion rate of the drawn wires is related to the presence of the deformation-induced $AgZn_3$ precipitates, which enhance micro-galvanic coupling. Because the depletion of Ag from the Zn matrix, the corrosion potential between diluted Zn matrix and precipitates is reduced, however previous studies demonstrated cold working in all metallic materials impairs corrosion resistance due to strain-induced crystalline defects, such as dislocations and twins. Present literature involves contradictory results in this regards, while quite rare studies about the corrosion behavior of ultrafine-grained zinc alloys were reported. Therefore, fundamental understanding of the corrosion behavior as well as contributed mechanisms the main challenges in this area which are yet to be addressed.

Conclusion

Zinc and its alloys serve as the next generation of temporary medical implant devices. However, their insufficient mechanical properties in the physiological environment may lead to premature failure of medical devices. Preliminary research evidences have proved that the drawbacks are tunable through combinations of different alloying elements and SPD processing conditions. Adding the alloying elements Li, Ag, Cu and Mg can result in high strength as well as improved ductility in SPD processed zinc alloys, while preserving the biocorrosion rate. SPD methods may assist in overcoming the limitation through grain refinement, particle strengthening, PSN, particle pining, twinning mechanisms. There remains large room for improvement in mechanical properties of zinc alloys to deal with uncertainties including low creep resistance, high susceptibility to natural aging, and static recrystallization at body temperature.

References

1. Bornapour M. Investigation of new biodegradable magnesium alloy with improved biocorrosion, biocompatibility and mechanical properties for use in temporary cardiovascular stents (Doctoral dissertation, McGill University).
2. Seitz J-M, Durisin M, Goldman J, Drelich JW. Recent Advances in Biodegradable Metals for Medical Sutures: A Critical Review. Advanced Healthcare Materials. 2015;4(13):1915-36.
3. Moravej M, Mantovani D. Biodegradable metals for cardiovascular stent application: interests and new opportunities. International journal of molecular sciences. 2011;12(7):4250-70.
4. Peuster M, Hesse C, Schloo T, Fink C, Beerbaum P, von Schnakenburg C. Long-term biocompatibility of a corrodible peripheral iron stent in the porcine descending aorta. Biomaterials. 2006;27(28):4955-62.
5. Katarivas Levy G, Goldman J, Aghion E. The Prospects of Zinc as a Structural Material for Biodegradable Implants—A Review Paper. Metals. 2017;7(10):402.
6. Mostaed E, Sikora-Jasinska M, Drelich JW, Vedani M. Zinc-based alloys for degradable vascular stent applications. Acta biomaterialia. 2018;71:1-23.
7. Bowen PK, Guillory RJ, 2nd, Shearier ER, Seitz J-M, Drelich J, Bocks M, et al. Metallic zinc exhibits optimal biocompatibility for bioabsorbable endovascular stents. Mater Sci Eng C Mater Biol Appl. 2015;56:467-72.
8. Vojtěch D, Kubásek J, Šerák J, Novák P. Mechanical and corrosion properties of newly developed biodegradable Zn-based alloys for bone fixation. Acta Biomaterialia. 2011;7(9):3515-22.
9. Čapek J, Kubásek J, Pinc J, Drahokoupil J, Čavojský M, Vojtěch D. Extrusion of the biodegradable ZnMg0.8Ca0.2 alloy – The influence of extrusion parameters on microstructure and mechanical characteristics. Journal of the Mechanical Behavior

of Biomedical Materials. 2020;108:103796.
10. Zhao S, Seitz J-M, Eifler R, Maier HJ, Guillory RJ, 2nd, Earley EJ, et al. Zn-Li alloy after extrusion and drawing: Structural, mechanical characterization, and biodegradation in abdominal aorta of rat. Mater Sci Eng C Mater Biol Appl. 2017;76:301-12.
11. Liu X, Sun J, Zhou F, Yang Y, Chang R, Qiu K, et al. Corrigendum to "Micro-alloying with Mn in Zn–Mg alloy for future biodegradable metals application" [Mater. Des. 94 (2016) 95–104]. Materials & Design. 2016;96:377.
12. Humphreys FJ, Prangnell PB, Priestner R. Fine-grained alloys by thermomechanical processing. Current Opinion in Solid State and Materials Science. 2001;5(1):15-21.
13. Torabi M, Eivani AR, Jafarian H, Salehi MT. Re-strengthening in AA6063 Alloy During Equal Channel Angular Pressing. Journal of Ultrafine Grained and Nanostructured Materials. 2017 Dec 1;50(2):90-7.
14. Veena P, Yadav DM, Kumar CN. A critical review on severe plastic deformation. IJSRSET. 2017;3(2):336-43.
15. Cao Y, Ni S, Liao X, Song M, Zhu Y. Structural evolutions of metallic materials processed by severe plastic deformation. Materials Science and Engineering: R: Reports. 2018;133:1-59.
16. Fatemi M, Zarei-Hanzaki A. Review on ultrafined/ nanostructured magnesium alloys produced through severe plastic deformation: microstructures. Journal of Ultrafine Grained and Nanostructured Materials. 2015 Dec 1;48(2):69-83.
17. Mohammad Nejad Fard N, Mirzadeh H, Mohammad R, Cabrera JM. Accumulative roll bonding of aluminum/stainless steel sheets. Journal of Ultrafine Grained and Nanostructured Materials. 2017 Jun 1;50(1):1-5.
18. Gu X-N, Zheng Y-F. A review on magnesium alloys as biodegradable materials. Frontiers of Materials Science in China. 2010;4(2):111-5.
19. Gong H, Wang K, Strich R, Zhou JG. In vitro biodegradation behavior, mechanical properties, and cytotoxicity of biodegradable Zn-Mg alloy. J Biomed Mater Res B Appl Biomater. 2015;103(8):1632-40.
20. Bowen PK, Seitz J-M, Guillory RJ, Braykovich JP, Zhao S, Goldman J, et al. Evaluation of wrought Zn-Al alloys (1, 3, and 5 wt % Al) through mechanical andin vivotesting for stent applications. Journal of Biomedical Materials Research Part B: Applied Biomaterials. 2017;106(1):245-58.
21. Niu J, Tang Z, Huang H, Pei J, Zhang H, Yuan G, et al. Research on a Zn-Cu alloy as a biodegradable material for potential vascular stents application. Materials Science and Engineering: C. 2016;69:407-13.
22. Tang Z, Niu J, Huang H, Zhang H, Pei J, Ou J, et al. Potential biodegradable Zn-Cu binary alloys developed for cardiovascular implant applications. Journal of the Mechanical Behavior of Biomedical Materials. 2017;72:182-91.
23. Jia B, Yang H, Han Y, Zhang Z, Qu X, Zhuang Y, et al. In vitro and in vivo studies of Zn-Mn biodegradable metals designed for orthopedic applications. Acta Biomaterialia. 2020;108:358-72.
24. Dai Y, Zhang Y, Liu H, Fang H, Li D, Xu X, et al. Mechanical strengthening mechanism of Zn-Li alloy and its mini tube as potential absorbable stent material. Materials Letters. 2019;235:220-3.
25. Li G, Yang H, Zheng Y, Chen X-H, Yang J-A, Zhu D, et al. Challenges in the use of zinc and its alloys as biodegradable metals: Perspective from biomechanical compatibility. Acta Biomaterialia. 2019;97:23-45.
26. Dambatta MS, Izman S, Kurniawan D, Hermawan H. Processing of Zn-3Mg alloy by equal channel angular pressing for biodegradable metal implants. Journal of King Saud University - Science. 2017;29(4):455-61.
27. Bednarczyk W, Kawałko J, Wątroba M, Bała P. Achieving room temperature superplasticity in the Zn-0.5Cu alloy processed via equal channel angular pressing. Materials Science and Engineering: A. 2018;723:126-33.
28. Wang L, He Y, Zhao H, Xie H, Li S, Ren Y, et al. Effect of cumulative strain on the microstructural and mechanical properties of Zn-0.02 wt%Mg alloy wires during room-temperature drawing process. Journal of Alloys and Compounds. 2018;740:949-57.
29. Guo P, Li F, Yang L, Bagheri R, Zhang Q, Li BQ, et al. Ultra-fine-grained Zn-0.5Mn alloy processed by multi-pass hot extrusion: Grain refinement mechanism and room-temperature superplasticity. Materials Science and Engineering: A. 2019;748:262-6.
30. Liu H, Huang H, Zhang Y, Xu Y, Wang C, Sun J, et al. Evolution of Mg–Zn second phases during ECAP at different processing temperatures and its impact on mechanical properties of Zn-1.6Mg (wt.%) alloys. Journal of Alloys and Compounds. 2019;811:151987.
31. Bednarczyk W, Wątroba M, Kawałko J, Bała P. Can zinc alloys be strengthened by grain refinement? A critical evaluation of the processing of low-alloyed binary zinc alloys using ECAP. Materials Science and Engineering: A. 2019;748:357-66.
32. Mostaed E, Sikora-Jasinska M, Ardakani MS, Mostaed A, Reaney IM, Goldman J, et al. Towards revealing key factors in mechanical instability of bioabsorbable Zn-based alloys for intended vascular stenting. Acta biomaterialia. 2020;105:319-35.
33. Liu S, Kent D, Doan N, Dargusch M, Wang G. Effects of deformation twinning on the mechanical properties of biodegradable Zn-Mg alloys. Bioact Mater. 2018;4(1):8-16.
34. Liao X, Wang J, Nie J, Jiang Y, Wu P. Deformation twinning in hexagonal materials. MRS Bulletin. 2016;41(4):314-9.
35. Bednarczyk W, Kawałko J, Wątroba M, Gao N, Starink MJ, Bała P, et al. Microstructure and mechanical properties of a Zn-0.5Cu alloy processed by high-pressure torsion. Materials Science and Engineering: A. 2020;776:139047.
36. Mostaed E, Ardakani MS, Sikora-Jasinska M, Drelich JW. Precipitation induced room temperature superplasticity in Zn-Cu alloys. Materials letters. 2019;244:203-6.
37. Jarzębska A, Bieda M, Kawałko J, Rogal Ł, Koprowski P, Sztwiertnia K, et al. A new approach to plastic deformation of biodegradable zinc alloy with magnesium and its effect on microstructure and mechanical properties. Materials Letters. 2018;211:58-61.
38. Ardakani MS, Mostaed E, Sikora-Jasinska M, Kampe SL, Drelich JW. The effects of alloying with Cu and Mn and thermal treatments on the mechanical instability of Zn-0.05Mg alloy. Materials Science and Engineering: A. 2020;770:138529.
39. Humphreys FJ, Hatherly M. Recrystallization and related annealing phenomena. Elsevier; 2012 Dec 2.
40. Huang H, Liu H, Wang L-S, Li Y-H, Agbedor S-O, Bai J, et al. A High-Strength and Biodegradable Zn–Mg Alloy with Refined Ternary Eutectic Structure Processed by ECAP. Acta Metallurgica Sinica (English Letters). 2020.
41. Sun S, Ren Y, Wang L, Yang B, Li H, Qin G. Abnormal effect of Mn addition on the mechanical properties of as-extruded Zn alloys. Materials Science and Engineering: A. 2017;701:129-33.
42. Zberg B, Uggowitzer PJ, Löffler JF. MgZnCa glasses without clinically observable hydrogen evolution for biodegradable implants. Nature Materials. 2009;8(11):887-91.
43. Bowen PK, Drelich J, Goldman J. Zinc Exhibits Ideal Physiological Corrosion Behavior for Bioabsorbable Stents. Advanced Materials. 2013;25(18):2577-82.
44. Gollapudi S. Grain size distribution effects on the corrosion behaviour of materials. Corrosion Science. 2012;62:90-4.