SYNTHESIS AND OPTIMIZATION OF GRAIN-REFINED BIODEGRADABLE ZN ALLOYS FOR CONTROLLED DEGRADATION

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ABSTRACT

Along the way, investigations over the past few years have focused on developing new Zn-based alloys as future materials for medical implants due to the poor mechanical and degradation properties. Effective grain size control is a fundamental property of Zn-based alloys that has a significant impact on their mechanical properties and degradation rate through various methodical adjustments of the microstructure. In particular, these critical properties of Zn-based alloys largely depend on grains' size and distribution in the respective microstructures. The review article critically analyzes the influence of grain refinement and microstructure on the mechanical properties, biodegradability, and biocompatibility of Zn-based alloys. The article establishes the interdependence between microstructure, mechanical properties, degradation rate, and biocompatibility of both Zn and its alloys. We conclude integration of alloying and fabrication techniques can significantly control grain refinement in Zn-based alloys, and the use of innovative techniques such as dynamic recrystallization and inoculation can further improve the grain refinement process. Although the tensile strength of the Zn alloys remained relatively unchanged following varied immersion time, a substantial decrease in elongation was observed. The decreased elongation primarily attributed to the formation of surface corrosion pits or holes, exacerbating crack propagation during tension.

Keywords: *Zn-based alloys, grain refinement process, biodegradability, mechanical and degradation properties*

INTRODUCTION

biodegradable metals are a new generation of materials which may be used in medical devices to improve patients' lives significantly. They can be used for producing temporary implants, which will dissolve in a human body after completing their mission of supporting the healing process of damaged tissue. Their degradation should proceed gradually with a harmless response from the host in regard to corrosive products. An example of an implant that does not require a long-term presence in a patient's body is a stent. This small, meshed tube used, among other things, in cardiovascular interventions supports artery walls and keeps the lumen open. Specialized application needs a number of properties such as biocompatibility, a steady corrosion rate, and the appropriate combination of mechanical strength and plasticity Pure Zn fulfils most of the aforementioned requirements, which makes it a very promising material for biodegradable stents. However, as-cast pure Zn has poor mechanical properties (i.e., yield strength, ultimate tensile strength, elongation to failure). Thus, it is of great importance to improve the strength and plasticity of pure Zn. Alloying is the most frequently applied method for strengthening biodegradable zinc, especially with elements such as magnesium, calcium or manganese. Very promising results were obtained for hypoeutectic Zn alloyed with Mg, where even a small addition of Mg yielded a significant increase in the mechanical strength of the as-cast material. Moreover, the addition of Mg is justified by its excellent biocompatibility. However, alloying alone does not meet high criteria for application in biodegradable implants. Therefore, it is often supported by methods of conventional plastic deformation, in particular hot rolling or hot extrusion. A combination of these two methods yielded further improvement in strength, but failed to deliver simultaneous enhancement of all mechanical properties above a rigorous limit. Another solution lies in the use of unconventional methods of plastic deformation. The number of papers concerning the use of severe plastic deformation (SPD) techniques with Zn and its alloys is rising. Lately, equal channel angular pressing (ECAP), high pressure torsion, the KoBo method and hydrostatic extrusion have been proposed. Hydrostatic extrusion is a technique allowing intensive plastic deformation, but is an unconventional SPD technique as the reduction in the cross-section of a material during the process occurs. One of the advantages of the method is a complex stress state due to hydrostatic pressure, which enables even hard-to-deform materials to be processed and crack formation to be suppressed effectively. Moreover, high deformation rates promote the accumulation of structural defects and, in consequence, grain refinement, which is of great importance in the case of Zn and its alloys characterized by relatively low recrystallization temperature. Grain refinement is determined by true strain, which is related to the reduction in a cross-section of a deformed material, which can be ensured in a single or multi-pass way. Our first results showed that hydrostatic extrusion, especially combined with magnesium alloying, can be suitable for obtaining materials that meet high requirements for biodegradable stents adding different magnesium content and increasing the number of passes leads to grain refinement and strengthens Zn-Mg alloys. However, to determine the optimum values for mechanical properties, further microstructure and texture investigations of hydrostatically extruded low-alloyed zinc are necessary. Detailed microstructural characterization is of great significance in order to provide a better understanding of strengthening mechanisms and to control the mechanical properties of newly developed materials.

LITERATURE REVIEW

Linjun Huang (2025) Orthopedic implants provide structural support, loading-bearing, or motion preservation to ensure surgical success. Zinc (Zn)-based alloys have emerged as promising candidates for next-generation orthopedic implants due to their suitable degradation rate, excellent mechanical properties, antibacterial activity, and complete degradability. However, the clinical application of Zn-based alloys is hindered by significant limitations, including mechanical instability, threshold-dependent bioactivity, an inadequate balance between antimicrobial and osteogenic effects, and variability in stress-induced degradation. This comprehensive review summarizes the feasibility of Zn-based alloys for orthopedic implants, focusing on the biocompatibility, biodegradation behavior, mechanical properties, and interactions with the resident cells. The engineering methods to modify properties of Zn-based materials are also discussed, and their translational applications are highlighted, while addressing the remaining challenges for future investigation. Collectively, advancing research in Zn-based alloys would pave the way for innovative orthopedic solutions that enhance patient outcomes.

Jie Cui et.al (2024) Laser Powder Bed Fusion (LPBF) is a widely used metal additive manufacturing technology that offers significant advantages in the precise fabrication of personalized geometric shapes and intricate porous structures for medical devices. Degradable zinc (Zn) alloys, as emerging biomaterials, hold great potential for clinical applications due to their excellent biocompatibility and suitable degradation rates. Recent advancements in the development of LPBF-fabricated Zn alloys have led to notable progress, particularly in orthopedic and cardiovascular applications. This review highlights the latest developments in the LPBF of Zn alloys, focusing on metallurgical defects, process parameters, microstructural features, mechanical properties, and degradation behavior. Specifically, it examines the types and formation mechanisms of metallurgical defects in LPBF-fabricated Zn components, along with strategies for their mitigation. The review systematically elucidates the grain structure, texture evolution, and elemental segregation that occur during the LPBF process. Furthermore, the influence of microstructural evolution and macroscopic porous structures on mechanical properties, degradation behavior, and biocompatibility is thoroughly analyzed.

Wang Heng et.al (2023) As biodegradable materials for biomedical purposes, people have done a lot of research on Mg alloy and Fe alloy. However, both types of materials have obvious shortcomings. Fe alloy has a very slow degradation rate due to the good protective effect of its degradation products, resulting in similar problems to non-degradable material. In this situation, Zn alloys are often mentioned in recent years, because Zn is an essential trace element for the human body, and the standard potential of Zn is between Mg and Fe, so its degradation rate is excellent. At the same time, Zn-based alloy has become a new biodegradable biomedical material after Mg alloy and Fe alloy, and has been widely used in cardiovascular stents, bone implants and internal fixation devices, and gastrointestinal staplers. At present, there is no systematic research result on biodegradable biomedical Zn-based Alloy Materials, the research interests include composition design, processing and preparation, degradation principle, biocompatibility, mechanical properties in all aspects. This article reviewed the properties of Zn-based Alloy Materials compared with other typical alloys and pointed out the future development direction.

Tian Huang et.al (2021) As a new kind of biodegradable metal, Zn possesses promising features, i.e. suitable biodegradability and biocompatibility, lower energy consumption for melting, better recyclability, and processing size tolerance. Such features provide some new insights for manufacturing medical implants. However, cast pure Zn usually contains coarsening microstructures, which brings about poor syngenetic controlling between mechanical strength and degradation rate. In the present work, a significant grain refinement was achieved in the Zn alloys through combination of solidification and rolling, followed by exploration of the mechanical response and in vitro degradation. Specifically, the grain refiner (i.e. Zn-Al master alloy) was firstly prepared and, then, added into cast pure Zn during solidification. Then, the cast Zn alloys were subjected to hot rolling at 200 °C, which gives rise to further reduction in the grain size of Zn alloys. Thereafter, the mechanical properties and the in vitro immersion testing were carried out not only in the as-rolled Zn-Al alloys, but also in the purely cast Zn-Al alloys for comparison.

N. Mollaei et.al (2020) 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 bio alloys to achieve acceptable mechanical characteristic while retaining their desired bio corrosion behavior. Summarizing present literature implied that Mg, Ag, Mn, and Ca containing zinc bio alloys 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

Grain refinement

Deformation of zinc alloy is governed by a variety deformation mode including basal, pyramidal and twinning systems. At the absence of enough slip systems, twinning is found to occur. 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 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. 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.

Zinc-based alloys for biodegradable stents

Zinc based alloys have been developed and investigated as possible candidates for bioabsorbable stent applications due to their nearly ideal biodegradation rate and acceptable biocompatibility. Zinc is an essential element for biological functions in nucleic acid metabolism, signal transduction, apoptosis regulation, gene expression, and endocrine regulation apart from interacting with a wide range of organic ligands. Zinc could potentially reduce the major problem of in-stent restenosis, which can cause stent implant failure. The degradation of iron was found to be too slow, while the degradation rate of magnesium is too fast as a potential biodegradable material for stent applications. The degradation problem associated with Mg and Fe could be avoided by using zinc and its alloys. . In recent years, several new biodegradable zinc based alloys have been developed to improve the mechanical properties of zinc alloys in order to facilitate their application as endovascular stents, either by altering the composition of alloying elements or by modifying the microstructure.

Processing Route and Technique for Property Improvement of Biodegradable Zinc Alloys

In developing material for a particular application, there is always a present goals of property requirements such materials must possessed for optimum performance in service. By so doing, the influence of processing route and constituting elements on material development cannot be over-emphasized. Similar is the development of biodegradable zinc alloys and composites to meeting the yearning properties requirement in medical industry. This section therefore, provides an outlook for latest processing route and various strategies that had been adopted for improvement of properties of zinc alloys. Reported that incorporation of alloying elements and/or appropriate processing techniques such as special casting, extrusion, rolling, forging and thermal treatments constitute efficient routes through which improvement in mechanical properties can be achieved. It must also be noted that suitable alloying elements that are non-toxic and capable of increasing strength must be carefully selected during synthesis of any implant BDMs.

Windows of Opportunities in Processing of Biodegradable Zinc Metals

The paradigm shift in biodegradable metals has received boosts in zinc metal research due to its moderate biodegradability and excellent biocompatibility properties as well as promising mechanical integrity which deteriorate at the healing pace of bone in bodily fluid over magnesium and iron metals. However, insufficient mechanical properties of pure zinc have been the fundamental limitation of its application in orthopaedic application. But findings from previous studies indicated that a careful selection of material design and processing route for zinc alloys/composites fabrication can annihilates the challenge of its poor mechanical properties. This implies that, there is a green light at the end of the tunnel for commercial clinical acceptability of biodegradable zinc metals for the repair or replacement of damaged or diseased bone. Illustrates the various windows of opportunities at researchers' disposal that has and/or can be adopted for the processing of a viable clinical required biodegradable zinc. Current literature.

Zn alloy powders

The quality and performance of LPBF-fabricated Zn alloy parts largely depend on the characteristics of the metal powder raw material. Metal powder with excellent flow ability ensures the formation of thin, uniform, and dense layers on the LPBF powder bed, facilitating efficient laser energy absorption. However, its behavior is significantly influenced by particle characteristics such as shape, size, distribution, moisture content, and static charge. For instance, rough particle surfaces can hinder flow and reduce distribution uniformity, leading to energy dissipation through multiple reflections under laser radiation. Non-spherical particles can disrupt reflection paths, affecting the precision of the formed sample. In contrast, spherical and smooth particles reduce inter-particle friction, enhancing flow, spread ability, and packing density on the powder bed, significantly reducing defects like porosity. Additionally, moisture in the powder increases viscosity and promotes aggregation, negatively affecting flow ability. Therefore, before introducing the powder into LPBF, the drying process is essential to ensure the forming quality of printed Zn alloy samples.

METHODOLOGY

Supplementary publications such as were mined for 1182 samples of Zn alloys. According to prior research, a biodegradable Zn alloy with effective corrosion and mechanical resistance qualities intended for medicinal uses would comprise several key constituents. Therefore, several columns containing non-essential elements such as (Nickel) Ni, Fe, Sc (Scandium), Tb (Test-Dreven), Sr, and Er (Erbium) were removed from the dataset to improve the efficacy and precision of the proposed models' predictions. Zn, Ca, Mn, Mg, and Li are the principal elements covered in the dataset. These optimized parameters are subsequently employed to construct the final XGBoost model, which is used to predict the mechanical properties of Zn alloys. The final stage is to create a biodegradable Zn alloy with the requisite mechanical properties. This investigation centered on the three essential mechanical characteristics of Zn alloys. Based on the recent data obtained, the most accurate model for forecasting the composition of the Zn alloy with the specified mechanical characteristics was selected.

RESULTS AND DISCUSSIONS

The alloy compositions were prepared by gravity casting under an argon atmosphere. The as-cast samples were conventionally extruded at 250 °C. Then, the samples were hydrostatically extruded to reduce the grain size and to compose both alloy phases. The highest degree of refinement was achieved by deformation and the synergistic effect of cumulative hydrostatic extrusion.

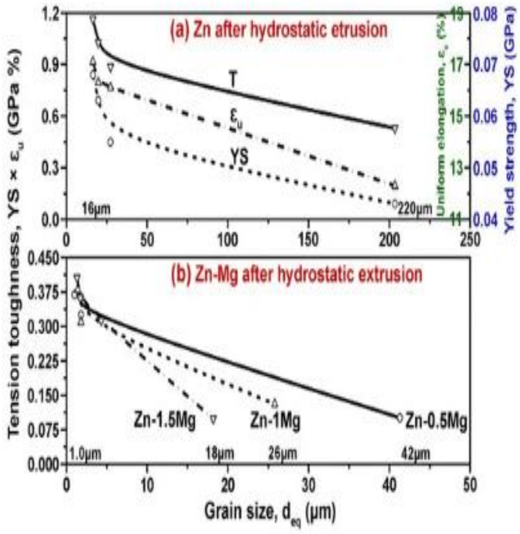

Figure 1. Variation in toughness with grain size distribution for (a) Zn and (b) Zn–Mg alloys. Reprinted with modification and permission from

It was suggested that three to four passes of hydrostatic extrusion are effective for minimizing the maximum temperature of the plastic deformation process. The uniform distribution of alloy phases plays a more important role in the enhancement of mechanical properties. The variation in toughness, with varying grain sizes for Zn-based alloys, is presented in Figure 1.

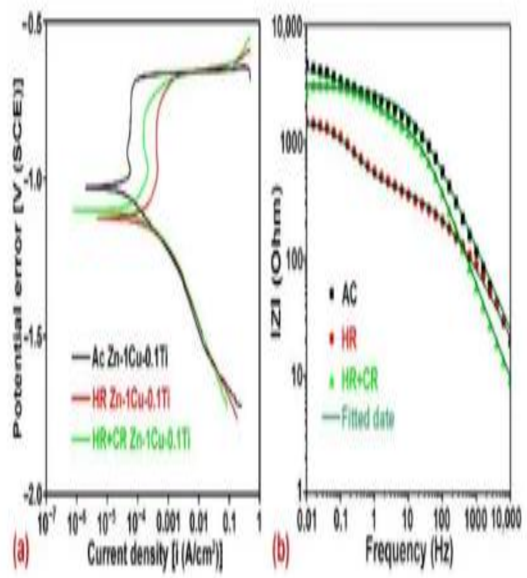

Figure 2. Immersion test results of Zn alloys: (a) polarization curves and (b) bode impedance modulus curves. Reprinted with changes and permission

In vitro and in vivo studies are performed to analyze the corrosion and degradation performance of Zn-based biodegradable materials. developed different compositions of Zn–1Cu–0.1Ti alloys by casting. The corrosion behavior was assessed from the polarization curves of alloys, which are displayed in Figure 2a. The maximum corrosion was recorded for hot-rolled specimens in terms of both the corrosion current and corrosion density. The minimum passive layer formation on the surface of Zn alloys was associated with the decreased dissolution rate. Figure 2b illustrates the impedance for all Zn alloys. The larger values of impedance indicate an improvement in corrosion resistance.

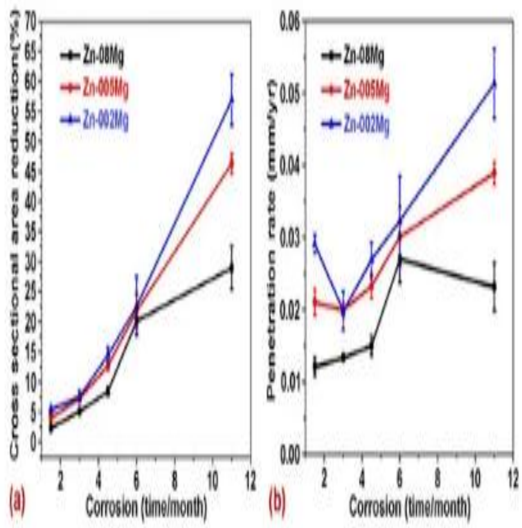

Figure 3. Degradation behavior: (a) cross-sectional area reduction and (b) penetration rate. Reprinted with modification and permission

developed the different Zn–Mg alloy compositions including the Zn–0.08Mg, Zn–0.005Mg, and 0.002Mg. The as-cast alloys were further extruded and drawn to improve the microstructure. In vivo studies were performed using Sprague-Dawley rats. The samples were placed within the arterial extracellular matrix for a period of 1.5, 3, 4.5, 6, and 11 months. The cross-sectional area reduction and penetration rate were measured to access degradation behavior. The degradation behavior in terms of cross-sectional area and penetration rate is shown in Figure 3. The degradation rate values evaluated from the penetration rate were higher for all compositions but close to the benchmark value (0.02 mm/y).

CONCLUSION

The microstructural feature, mechanical properties, and in vitro degradation were individually explored in the biodegradable Zne Al alloys. The pure Zn shows very large coarsening microstructure. Grain refiners and rolling treatment significantly promote the columnar-to equiaxed transition. The present work implies that the synergic controlling be-tween strength and degradation of Zn alloys can be well achieved through fine-grained manufacturing. Some of the fundamental obstacles to the use of biodegradable Mg and Fe appear to be overcome by Zn and its composites, and there has been increasing research on Zn metal in recent years. This paper reviews the current state-of-the-art on biodegradable Zn, including current advances, existing opportunities, and future research goals. The review focuses on the analysis of the microstructure, the mechanical and biological properties of Zn-based alloys and composites, as well as the alloying and fabrication processes. Zn demonstrates excellent corrosion rates and is suitable for bioresorbable implants. However, its poor mechanical properties have limited its medical applications. Adding alloying elements and reinforcements to Zn can have an important effect on improving its mechanical behavior.

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