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Review Article

A Short Review on Absorbable Zinc for Implant Applications

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The demand for absorbable and biodegradable materials for various biomedical applications has increased in recent decades. Absorbable materials eliminate the need for secondary surgery and reduce the complications and inflammation associated with traditional implant materials. Magnesium, iron, and zinc are the most commonly used biodegradable materials for addressing these issues. Zinc is an essential vital mineral of the human body, as it aids most of cellular functions. Zinc-based alloys are gaining importance because of their tunable mechanical properties, ease of processing, biodegradation rates, and biocompatibility. This review article highlights the use of zinc for implant applications.

Introduction

Bones are among the most active tissues in the human body and are self-regenerative. Advances in lifestyle, population aging, metabolic diseases, sports, and accidental injuries have led to bone defects. Bone grafting methods commonly address bone defects, fractures, tissue regeneration and repairs. Based on the nature of the injury, bone properties can be mimicked using autografts, allografts, or engineered biomaterials. The comparison of the properties of natural bone with those of commonly used biomaterials for implant applications is listed in table 1.

The structural capability and durability of the scaffold depend on the mechanical properties such as elastic modulus, tensile strength and stiffness of the material used [7]. Biomaterials are engineered or naturally available materials used over a long period to repair, enhance tissues or organs of the human body through biomedical applications such as implants, stents, sutures, screws, staples, and bone plates. Metals, polymers, and ceramics have been widely used in various biomedical applications. Compared to metallic materials, polymers exhibit inadequate mechanical properties, slower tissue reconstruction, poor inflammatory responses, and subsequent cytotoxicity. Metallic biomaterials can be either nondegradable or biodegradable. Conventional nondegradable metals are employed because of their exceptional mechanical strength and corrosion resistance. Effects such as stress shielding, loosening after implantation, mismatch of strength with natural bone, inflammation, and poor biocompatibility necessitate secondary surgery post-implantation. Absorbable/biodegradable metals or their alloys can overcome the need for secondary surgery. These materials exhibit excellent mechanical properties, corrosion behavior, bioactivity, osteoconductivity, osteoinductivity, biodegradability, and biocompatibility [8].

Absorbable/Biodegradable Materials

Major essential traces of metallic elements, such as calcium and magnesium, along with minor traces of Cr, Mn, Fe, Co, Ni, Cu, Zn, and Mo, are indispensably present in the human body in varying quantities. Iron (Fe), magnesium (Mg), and zinc (Zn) are widely used as absorbable base metals. These elements are necessary and compatible with human body cells and tissues, as they aid in metabolic functions. Alloying of these non-toxic metals was performed to improve their properties. Iron is an essential nutrient for the human body and aids several enzymatic functions. Iron possesses excellent mechanical properties, formability, and biocompatibility, but exhibits excessively slow degradation rates. Alloying of Fe enhances these properties. Magnesium and its alloys are lightweight and have a low elastic modulus and high specific strength relative to other biodegradable metals (BMs). Hydrogen gases are evolved at the interface region between the surrounding tissue and the implant during biodegradation of magnesium-based alloys, leading to the formation of an interfacial gas pocket, thus influencing in vivo application of the alloys. The pockets formed thereby reduce interfacial stability, accelerate early failure and micromotion, thus affecting the load-bearing applications of the implant [9-10]. Therefore, in comparison to iron-based and magnesium-based BMs, zinc and its alloys are gaining importance as the next generation absorbable materials for bone tissue engineering [8].

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Table 1: Comparison of properties of natural bone with biomaterials [1-6]

Material	Density (g/cm³)	Elastic Modulus (GPa)	Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	Elongation (ε) (%)	Degradation rate (mm y^{-1})
Natural Cortical Bone	1.8–2.1	3–20	130–193	35–283	3–7	Natural bone remodeling
Pure Mg	1.74–2.0	41–45	65–100	135–285	7–40	0.8-2.7
Pure Fe	7.8	213		300	37.5	0.1
Pure Zn	7.1	78–121	~21–30	97–150	~0.3–2	0.1-0.3
Ti alloy	4.4–4.5	110–127		900–1000	10-15	No
Stainless Steel	7.9–8.1	189–205	170–310	460–1700	10–40	No
PEEK	1.30	3–4	90–100	90–100	20–40	No
Co–Cr Alloy	8.3–9.2	~230	450–1000	~860–1540	~20–30	No

Zinc as an Absorbable Material

Zinc is a very fundamental element of the human body. Zinc plays a crucial role in cell proliferation, stimulation of new bone formation, anti-inflammatory effects, and other biological functions, including wound healing. Zn is a shiny bluish-white metal with a melting point of 419.5°C and a density of 7.13 g/cm^3 [11]. Pure Zinc exhibits limited mechanical properties, regardless of the processing method used. As-cast pure Zn exhibits a tensile strength of 18 MPa, with fracture elongation of 0.32% [12]. Zn has a hexagonal close-packed (HCP) crystal structure. The basic functions that determine the utilization of Zn in biomedical applications are: (1) the significance of Zn for all life forms, (2) Catalytic and structural functions of Zn in enzymes and proteins, and (3) Zn as an indicator mediator in cells. Mechanical behaviors such as creep, strength, ductility, cyclic, and corrosion fatigue have a significant impact on the biodegradability of zinc-based alloys [13-14]. The alloying of zinc with different elements, such as aluminum (Al), calcium (Ca), magnesium (Mg), lithium (Li), and silver (Ag), improves its properties, including osteogenic promotion, antibacterial properties, immunomodulation, and mechanical properties [12]. Alloying aids in more dislocation slip systems, increases lattice dislocation density, thereby enhancing the resistance of the dislocation motion [15]. Since 3000 BC, Zn has been commonly alloyed with Cu. This alloy is known as brass. The addition of lithium (Li) to zinc enhances mechanical strength[16]. Ductility was found to be retained more in zinc-based alloys when compared with pure Zn [17].

Biodegradability

The performance of any absorbable material depends on its degradation behavior. Zinc has a standard corrosion potential of - 0.76 V. This potential value of the corrosion lies between the two commonly used degradable materials, namely Fe (-0.44 V) and Mg (-2.37 V). Thus Zn-based BMs exhibit intermediate degradation rates between the Mg-based and Fe-based BMs. Depending on the pH of the solution used, the degradation mechanism of zinc involves both redox and oxygen reduction reaction.

Electrochemical corrosion of Zn under physiological conditions. Zinc is thermodynamically unstable in aqueous solutions, tend to dissolve, and loses two electrons at the anode.

$$Zn = Zn^{2+} + 2e^-$$

H^+ ions are generated during the hydrolysis of Zn^{2+} ions, leading to slight acidification of the anodic sites. The kinetics of the reactions are independent of the solution pH, resulting in direct oxygen consumption at the Zn metal interface.

$$Zn + H_2O = ZnOH^+ + H^+$$

Hydroxide is produced during the reduction reaction in the electrolyte.

$$O_2 + 2H_2O + 4e^- = 4OH^-$$

The instantaneous increases of Zn^{2+} and OH^- in the solution accelerate the precipitation of unstable Zn $(OH)_2$, which is formed on the surface of Zn metal in neutral to slightly alkaline solutions. Zinc hydroxide transforms into thermodynamically more stable ZnO. This transformation can be explained through various mechanisms, namely, the dissolution–reprecipitation mechanism, in situ crystallization, and solid–solid phase transformation.

$$Zn^{2+} + 2OH^- = Zn(OH)_2$$

$$Zn(OH)_2 = ZnO + H_2O$$

$$ZnO + H^+ = ZnOH^+$$

The hydroxide layer formed acts as a buffering or protective phase on the surface. The dissolution of this results in the accumulation of ions resulting in variation of pH, ionic strengthening, and surface chemistry. At body temperature, the slow dehydration of Zn $(OH)_2$ aids the nucleation and growth of ZnO seeds. Dissolution–reprecipitation mechanism, in situ crystallization, and solid–solid phase transformation are the common mechanisms that help to understand phase transformations. Based on physiological conditions, the degradation products that are formed are ZnO, zinc phosphate, and zinc carbonate [18]. From the above reactions, it was observed that non-toxic and completely bioresorbable products are formed without hydrogen gas production during the degradation process [18-20]. This avoids the formation of hydrogen gas cavities, thereby enabling continuous and stable contact between the implant and tissue/bone [21].

Biocompatibility

Biocompatibility refers to the study of implant behaviors in biological systems [22]. 85% of the zinc is distributed in the different parts of the human body. Zinc is naturally obtained through diet. The daily dietary intake of Zn varies from 2 to 3 mg/day for infants and up to 8–11 mg/day for adults [20]. Zinc-based alloys are gaining popularity because of their proven biocompatibility *in vitro* cytotoxicity studies and *in vivo* studies in animals [22]. Biological activities such as bone remodeling, gene expression, enzymatic, and immune regulation are influenced by the Zn concentration. Zn^{2+} ions are released to surrounding environments and blood streams post implantation [23]. Even though Zn aids in various biological activities, its concentration affects biocompatibility. Uncontrolled release of Zn^{2+} ions concentration aids in localized cytotoxicity. Cytotoxicity threshold can be controlled by addition of various alloying elements to zinc. Alloying controls the rapid dissolution of zinc, thereby preventing the accumulation of localized Zn^2z ions [24-25]. Alloying also ensures excellent biocompatibility and corrosion resistance [24]. In *in vitro* experiments the cell response is determined by the quality and quantity of products formed during the degradation process[15,26]. In case of in vitro studies, one needs to revisit the existing ISO 10993 standard series for cytotoxicity assessment to consistently assess the degradability and biocompatibility of Zn-based alloys [23]. In humans, zinc deficiency leads to impaired skeletal development, severe anemia, skin abnormalities, mental lethargy, and impaired bone growth. The effects of Zn deficiency in humans are shown in the figure 1.

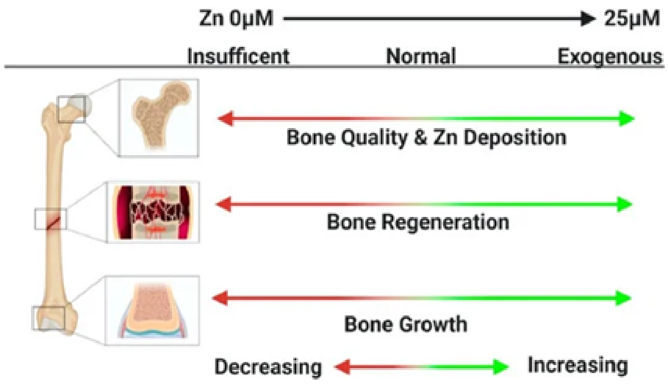

Figure 1: Effect of zinc deficiency in humans [19]. Reproduced from Liu et al. (2022) under the terms of the Creative Commons licence

Processing of Zinc and its Alloys

The fabrication and processing of engineered biodegradable metals and alloys play a critical role in the properties and material performance of biological environments. Various conventional and advanced techniques have been employed to develop absorbable Zn and its alloys. Some of the most used conventional techniques are casting, rolling, extrusion, drawing, and forging. Advanced processing techniques include severe plastic deformation, additive manufacturing (AM), electroforming, and spark plasma sintering [23,27-28]. Furthermore, the properties can be refined by performing post-processing treatment. Among the various processing techniques used for zn and its alloys, additive manufacturing is gaining popularity due to its tailoring capabilities, structure porosity, and controlled mechanical properties. The powder bed fusion (PBF) process is the most commonly used process among all other AM processes [18]. Lasers or electron beams are commonly used energy source for fusion and the melting of powders in the PBF process [29]. Even though LPBF is advantageous, major challenges are faced during the AM of Zn-based alloys using the LPBF process. This is mainly due to the low boiling point (907°C), leading to extreme evaporation, spattering, and pore formation during processing [22,30-31]. Parameters such as powder properties, laser power, scanning speed, precision, and layer thickness significantly affect the implant properties and biological behavior. Furthermore, the properties of the processed Zn-based alloys can be refined by performing the post-processing treatments.

Conclusion

In recent years, extensive research has been carried out to study the properties of various biodegradable materials, alloys, and composites for biomedical applications. The present article provides an overview of the use of zinc as an absorbable biomaterial for biomedical applications, owing to its ease of processing and fabrication, excellent mechanical properties, and biodegradation behavior.

Zinc is essential for the human body as it supports various biological functions, including bone regeneration, wound healing, etc. Alloying zinc with other elements enhances its mechanical strength, biocompatibility, and biodegradation. The degradation of zinc results in non-toxic and absorbable products without the evolution of hydrogen gas. Due to these factors, absorbable zinc-based materials are emerging as a promising alternative absorbable material for implant applications.

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