Laser Additive Manufacturing of Zinc Targeting for Biomedical Application

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Abstract: Biodegradable zinc (Zn) is expected to be used in clinical application like bone tissue engineering scaffolds, since it possesses favorable biocompatibility and suitable degradation rate. Laser powder bed fusion (LPBF), which is a typical additive manufacturing technique, offers tremendous advantages in fabricating medical devices with personalized geometric shape and complex porous structure. Therefore, the combination of LPBF and biodegradable Zn has gained intensive attention and also achieved rapid development in recent years. However, it severely challenges the formation quality and resultant performance of LPBF-processed Zn-based materials, due to the evaporation and element loss during laser processing. In this study, the current research status and future research trends for LPBF of Zn-based implants are reviewed from comprehensive viewpoints including formation quality, microstructure feature, and performance. The influences of powder characteristics and process parameters on formation quality are described systematically. The microstructure evolution, mechanical properties, as well as the degradation behavior are also discussed. Finally, the research perspectives for LPBF of Zn are summarized, aiming to provide guideline for future study.

Keywords: Additive manufacturing; Zinc implant; Formation quality; Microstructure; Mechanical properties

1. Introduction

Biomedical metallic materials have a long history of being used as implants such as bone fixation plate or screw, and cardiovascular stents, due to their comprehensive characteristics, including high strength, ductility, and favorable machinability¹⁻³. Particularly, biodegradable biometal including iron (Fe), magnesium (Mg), and zinc (Zn) have recently gained intensive attention⁴⁻⁶. They can be gradually degraded in vivo accompanying with the regeneration of new tissue, thus mitigating the pain of secondary surgery and economic burden on patients. Meanwhile, the released metal ions have no obvious adverse effect on surrounding host tissue⁷. It should be noted that Mg degrades too rapid in human body environment, due to its high electrochemical activity with a standard corrosion potential of −1.7 V⁸. As for Fe, it degrades too slowly⁹. It is reported that the full degradation of Fe implant takes about several years, and its degradation product is difficult to be dissolved¹⁰. Unlike Mg and Fe, Zn possesses a relatively moderate
degradation rate. In addition, Zn is a nutrient element for human body and serves an key role in protein synthesis, signal transduction, and normal functions of various enzymes, especially in strengthening human immunity and promoting wound healing\[^{11}\]. Therefore, a series of Zn-based materials have been developed for clinical application\[^{12-13}\].

Additive manufacturing, which integrates computer-aided design, material processing, and forming technology, shows great potentials in manufacturing accurate devices as compared with traditional processes\[^{14-16}\]. According to the American Society for Testing and Materials standard, it is divided into seven categories, including polymerization, material jet forming, material extrusion, powder bed fusion, binder spray forming, sheet lamination, and direct energy deposition. Among them, direct energy deposition and powder bed fusion are two main additive manufacturing techniques for metal parts. Comparing with direct energy deposition, powder bed fusion, particularly laser powder bed fusion (LPBF) technology, which uses laser beam as energy source, has small beam spot diameter, fine powder, and thin forming layer, therefore exhibiting relatively high dimensional accuracy\[^{17-19}\]. Completely different from conventional process like casting, LPBF is a near-net-shape fabrication technology which builds parts in means of layer-by-layer fashion\[^{20,21}\]. As high-energy laser radiates on the metallic powder, a microscale melt pool is formed, which subsequently undergoes a rapid solidification. Usually, a sharp temperature gradient and consequent high cooling rate even above $\sim 10^7$ K/s can be achieved within the melt pool\[^{22}\]. Therefore, the microstructure containing microscale grains and precipitates is generally established, which endows LPBF-processed parts with excellent comprehensive performance\[^{23,24}\].

In the last couple of years, the combination of LPBF and biomedical metals has received extensive attention in biomedical filed\[^{25-28}\]. Due to the rapid melting/solidification and unique domain-by-domain localized forming characteristics, LPBF is able to accurately regulate the material density, grain size, precipitate distribution, and texture strength, which are important for controlling the mechanical properties, degradation behavior, and biological response of metallic implants\[^{29}\]. On the other hand, it is able to customize the macro- and micro-structure with arbitrary complex shape and high precision\[^{30}\]. A three-dimensional interconnected porous structure which is similar to human bone can be easily built by LPBF, which is conducive to nutrient transport and the regeneration of damaged tissue. Montani et al.\[^{31}\] first explored the feasibility of LPBF Zn in 2017, and some encouraging results were achieved in mechanical properties as compared with as-cast Zn, which is believed to be caused by the small grain size obtained through the fast cooling cycle\[^{32}\]. Subsequently, Wen et al. unitized LPBF to prepared Zn scaffold for biomedical application in 2018. The degradation behavior and cell response were also preliminarily evaluated.

However, the evaporation of Zn easily occurs due to relatively low melting and boiling point. The gas entrapment and the retention of slight residual porosity are generally observed during LPBF of Zn, and seriously degrade the comprehensive properties of as-built parts\[^{33}\]. Investigations on powder properties and process parameters were carried out to address this issue, and some substantive progress was obtained\[^{32,34}\]. Nevertheless, an accurate microstructure control and a profound interpretation of the relationship between microstructure and performance are still a challenge up to now. In the present work, the factors that affect the formation quality of LPBF-processed Zn are comprehensively reviewed. The microstructure, mechanical performance, degradation behavior, and cytocompatibility were discussed systematically. This paper aims to guide the future research engaged in the application of Zn-based implants fabricated by LPBF.

2. Factors affecting the formation quality

2.1. Powder properties

High formation quality is the prerequisite of LPBF-processed Zn parts with stable mechanical properties and biological behavior. In general, the formation quality is primarily related to the powder properties and processing parameters\[^{35}\]. Table 1 shows the major intrinsic characteristics of Zn powder for LPBF\[^{36}\]. Zn has high density and promotes the movement of powder during LPBF, which reduces the interference of gas flow on powder layer. Its low surface tension and viscosity are able to improve the densification rate of as-built parts\[^{37}\]. However, Zn possesses relatively low melting and boiling point, resulting in a small and narrow forming window during LPBF. Moreover, the relatively low specific heat and high laser absorptivity of Zn powder usually result in a high evaporation tendency\[^{38}\].

Apart from the inherent properties, the formation quality is affected by the fluidity of Zn powder, which is attributed to the powder properties such as particle shape, size, and chemical composition. In general, spherical particles with low surface friction and mechanical interlock improve the fluidity and facilitate the uniform spreading of powder\[^{39}\]. On the other hand, the particle size distribution shifting to the direction of coarse particles cause high-energy absorption, thereby reducing the laser energy arrived the underlying surface\[^{40}\]. In this case, the thermal penetration depth is reduced and potentially results in inhomogeneous regions such as cracks and incomplete fusion\[^{40}\]. In contrast, fine particles...
are easily melted and increase the thermal penetration depth, thus improving the densification rate\cite{44}. It should be mentioned that the presence of surface-active elements in powder, such as oxygen and sulfur, is able to increase the thermal capillary force within the molten pool, which yields a huge surface tension gradient, and then triggers a relatively strong fluid circulation and instability in the molten pool\cite{42}.

At present, the suitable powders designed for LPBF are quite limited, which becomes one of the obstacles for LPBF of Zn. The powder requires proper rheological properties to form a thin, dense, and uniform powder layer. At present, the processing technologies of powders for LPBF technique include plasma, gas, and water atomization\cite{43-45}. Each processing technology can produce specific powder characteristics including morphology, particle size, and porosity, which significantly affects the rheological behavior of Zn powder. Demir et al.\cite{6} fabricated Zn powders by water atomization and sieved them into coarse powder (15 μm) and fine powder (9 μm), as displayed in Figure 1A and B. Compared with coarse powder, fine powder is relatively susceptible to the variation of laser energy input. Ruvalcaba et al.\cite{46} utilized water-atomized Zn powder, as shown in Figure 1C, to fabricate testing samples with a density of only 95% under the action of the optimized parameters. It is revealed that the water-atomized Zn powder is difficult to fabricate high-density samples, which is attributed to the forming of high oxygen content under the impact of water jet. The air-atomized Zn powders with elongated flake, stick shape, and minor portion of teardrop shape are exhibited in Figure 1D and E\cite{47}. The oxidation on the surface of the droplet can form oxide film, which prevents the spheroidization of the melt droplet during solidification. Wen et al.\cite{48} fabricated Zn parts using nitrogen atomized powder with spherical shape. Their results reveal that the spherical powder improves the powder fluidity and favors the deposition of uniform powder layer, thereby obtaining Zn parts with high densification.

### 2.2. Process parameters

Processing parameter, which directly determines the laser energy input, is the other important factor that affects the formation quality of LPBF-processed Zn. In general, the densification rate and surface quality are the two important indexes to estimate the formation quality of LPBF-processed parts\cite{49}. Excellent formation quality is also the key to preventing fatigue damage\cite{50,51}. Unfortunately, serious evaporation of Zn easily occurs during LPBF even at low laser energy input, which exerts a significantly negative influence on the formation quality. Due to the recoil force of evaporation, the molten pool moves violently and results in the ejection of massive Zn liquid from the molten pool, which will disturb the adjacent powders and then push the powders away from the molten pool\cite{52}. The melted Zn solidifies into spherical particles and adheres to the track surface under the action of surface tension, which eventually leads to the surface roughness deformation and density reduction of Zn-based materials.

The related process parameters mainly include laser power, scanning rate, hatching space, and layer thickness\cite{53}. In general, laser power affects the thermodynamics and temperature distribution of molten pool. As shown in Figure 2A, a limited portion of powder particles near the laser irradiation center area is obviously melted at relatively low laser power. Meanwhile, powder particles far from the irradiation region actually maintain their original spherical shape and point contact with each other. Apparently, the shell at the border of the powder particles is melted by laser beam. However, the core of the powder particles is not significantly affected and retains the initial solid state, which causes relatively high viscosity of liquid pool, thereby resulting in low melt flow capacity. As a result, the formed molten metal cannot diffuse completely, leaving a valley between two adjacent particles and a rough surface. As the laser power increases, the enhanced width generated in the molten pool significantly promotes the melt spreading ratio, which produces effective wetting ability and a desired metallurgical bonding with adjacent tracks. With the further increase of laser power, massive powder particles completely melt. Then, adjacent particles adhere to the molten pool, which causes a lack of powders in the adjacent area, thus resulting in the formation of pores and balling droplets that aggravate the surface roughness\cite{42}. Therefore, with the increase of laser power, the combined width of scanning trace and temperature within the molten

| Metal powders | Melting point (°C) | Boiling point (°C) | Specific heat (J/kg·K) | Surface tension (mN/m) | Laser absorptivity (%) | Density (g/cm³) |
|---------------|--------------------|--------------------|------------------------|------------------------|------------------------|------------------|
| Zn            | 420                | 907                | 382                    | 782                    | 70                     | 7.14             |
| Fe            | 1358               | 2862               | 444                    | 1835                   | 75                     | 7.87             |
| Mg            | 650                | 1091               | 1360                   | 559                    | \                      | 1.74             |

LPBF: Laser powder bed fusion

Table 1. The intrinsic characteristic features of Zn, Fe, and Mg powders used by LPBF

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pool generally enlarges, which results in the enhancement of bonding ability between adjacent traces.[5]

The scanning rate determines the interaction time between the laser beam and powder particles, which affects the laser energy input in the molten pool and densification of samples, as exhibited in Figure 2B. At a high scanning speed, the supplied heat provided by laser is insufficient to melt the whole particles, which leads to incomplete bonding. In this case, the surface tension causes the melt on the surface to shrink outward, and this fluid flow
breaks melt track into droplets, which eventually result in the Plateau–Rayleigh instability and the formation of opening defects\cite{58}. When the scanning speed decreases, this instability is alleviated. However, the molten metal solidifies before filling the pores due to the high thermal conductivity of metal powders, thus resulting in many keyhole pores and inverted triangle pores\cite{59}. With the further decrease of the scanning speed, the powder layer inside the laser radiation area is completely melted and then forms a complete molten pool. Specifically, the low scanning speed corresponding to the high laser energy input per unit length contributes to sufficient metallic liquid and high peak temperature in molten pool, so as to reduce the viscosity and surface tension. Flow capacity of melts is evidently enhanced due to low melt viscosity and surface tension caused by high working temperature\cite{60}. Consequently, the metallic liquid spreads wider and fills in the gaps between particles efficiently, which contributes to the decrease of the porosity and the improvement of formation quality.

The influence of powder layer thickness on surface structure and porosity rate should also be marked, which is realized by its influence on melt flow behavior\cite{61}. The powder layer thickness mainly affects the melt behavior by influencing the amount of material melted by laser beam. As the powder layer thickness increases, the melted powder materials increase and the melt surface area enlarges accordingly, which leads to high evaporation and Marangoni force\cite{62}. In this case, the melt flow velocity increases, which destroys the stability of melt flow. In addition, relatively thick powder particles largely consume the input laser energy, reducing the heat used for the remelting of previous layer. As a result, the freshly melted material cannot be well bonded to the previous layer, and more easily cause melt splashing and porosity. Considering the relatively thick powder layer that leads to highly irregular and unstable melt pools, selecting the appropriate powder layer thickness is the key to controlling the porosity and improves the formation quality\cite{63}. The hatching space also plays an important role in the formation quality of LPBF-fabricated samples\cite{64}. The hatch spacing is closely related to the laser spot diameter. In general, relatively small hatching space means massive overlapping remelting between scanning passes, leading to a large amount of evaporation, thus destroying the surface structure and reducing the formation quality. On the other hand, excessive hatching space leads to non-overlapping area, which cannot be melted completely and greatly reduces the formation quality.

To optimize the process parameters, the input of laser energy is expressed by the laser energy density ($E_v$) as follows\cite{65}:

$$ E_v = \frac{P}{(V \cdot d_s \cdot h_s)} \quad (1) $$

Where, the $P$, $V$, $d_s$, and $h_s$ are laser power, scanning rate, hatching space, and layer thickness, respectively. Basing on the Equation 1, the process window for Zn powder with varied $P$ and $V$ through massive tests is obtained, as displayed in Figure 3A. When the laser energy density is 60–135 J/mm$^3$, the Zn evaporation decreases and the density of laser melted parts reaches

Figure 3. (A) The densification under different laser energy input for Zn. Reprinted from Materials & Design, 155, Wen P, Voshage M, Jauer L, et al., laser additive manufacturing of Zn metal parts for biodegradable applications: Processing, formation quality and mechanical properties, 36-45, Copyright (2018), with permission from Elsevier\cite{48}. (B) The processing map of LPBF experiments and corresponding surface morphology for Zn-Al parts. Reprinted from Journal of Alloys and Compounds, 798, Shuai C, Cheng Y, Yang Y, et al., laser additive manufacturing of Zn-2Al part for bone repair: Formability, microstructure, and properties, 606-615, Copyright (2019), with permission from Elsevier\cite{32}. 78 International Journal of Bioprinting (2022) – Volume 8, Issue 1
99.5%. According to different regions of the processing window, the Zn-Al parts are also fabricated, as exhibited in Figure 3B. It is found that reasonable laser energy density can reduce the Zn evaporation degree and improve the formation quality. Notably, under optimized process parameters, rare earth elements (REs) like neodymium (Nd) can release a large amount of heat, which reduces the liquid temperature and creates a narrow crystallization interval during LPBF\cite{66}. Meanwhile, REs as surface active elements are also able to deoxidize and purify the molten pool\cite{67}. As a consequence, evaporation of Zn is reduced and the fluidity is raised, thereby improving the formation quality of laser metal Zn parts.

Apart from the process parameters, the scanning strategy also has a significant effect on the formality of LPBF-processed parts. Usually, the rapid movement of laser beam and high-energy input at the local zone results in sharp changes in temperature distribution and temperature gradient during LPBF\cite{68}. As a result, high residual stress and uneven deformation may be produced. At present, several teams of researchers reported that one alternative linear hatching scanning strategy was used in LPBF of Zn\cite{69-71}. It is believed that such scanning strategy is able to reduce the residual stress and is easy to be generated from a computer-aided design file. However, the influence of different scanning strategy on formability is rarely studied for LPBF of Zn, which should be one issue worthy of attention in the future research. Particularly, LPBF of Zn, instead of other metals such as Fe or titanium, is more likely to cause gasification and smoke\cite{72,73}. Therefore, a more appropriate scanning strategy can be considered to reduce the interference of smoke on the laser beam, so as to improve the stability of molten pool.

2.3. Gas flow

LPBF is conducive to adjusting the performance of metal implants as compared with traditional manufacturing process\cite{74}. However, during laser process, the evaporation of Zn easily results in strong and uneven vapor flow in the molten pool\cite{74}. This situation can accelerate the irregular jump of molten liquid, resulting in serious spatter and the formation of pores, thus reducing the formation quality and corrosion resistance of the LPBF-processed samples, as displayed in Figure 4. In fact, numerous small particles exist in the evaporation fume of melted Zn. Such an evaporation fume will undoubtedly contaminate the transmission mirror and thereby disturb the propagation of the laser beam. As a result, the inaccurate laser beam with unstable laser energy or deviated direction sharply deteriorates the formation quality. A typical example is that a large number of keyholes are observed in the Zn matrix\cite{75}.

To reduce or even eliminate the impact of metal vapor on formation quality, Wen et al.\cite{77} developed an optimized gas circulation system to eliminate the negative effect of evaporation by numerical analysis. Results show that a stable LPBF process was achieved to prepared high-density porous Zn scaffolds under suitable blow-off and suction. Jauer et al.\cite{78} first adopted a specialized gas circulation system to remove the evaporation particles within the processing chamber during LPBF, thereby reducing the negative impact of the metal evaporation fume on formation quality and providing a stable processing environment. Based on this foundation, a gas circulation system was specially designed to prepare pure Zn during LPBF, and the influence of gas flow system design on the elimination of evaporated fume was numerically simulated. The results show that partial evaporated fume was effectively sucked out. Specially, the flowing inert gas generated directional flow in the cavity, which absorbed the evaporation products near the laser melting zone to prevent the contamination of the transmission mirror. As a result, the side effects of falling spatters on the next scanning track were decreased. It is ascribed to the fact that the quick and efficient removal of the evaporation products can void the attenuation of laser energy, thereby maintaining the stability of laser melting Zn-based materials and inhibiting the retention of gas in the molten pool. Meanwhile, the flowing argon atmosphere is able to provide appropriate pressure and prevent the formation of oxide layers on the pool, thereby reducing the fluctuation of molten metal in the molten pool and consequently improving the formation quality. As a result, the relative density of as-built Zn is >99%\cite{79}.

3. Microstructure and mechanical properties

3.1. Microstructure

The optimized laser energy input condition and gas shielding are used to fabricate Zn-based implants with a satisfactory quality. They possess special microstructure characteristics, such as fine grain, random grain orientation, and homogeneous texture. Usually, the fastest heat dissipation direction of the molten pool is perpendicular to the substrate, which leads to a high cooling speed of \(-10^4 \text{ – } 10^6 \text{ K/s as compared with the traditional casting process (}\sim 10^2 \text{ K/s})\text{. Therefore, a typical feature like the columnar grain along the building direction is present in the LPBF-fabricated Zn samples, although significant diversity in the microstructure decided by the process parameters is involved. Qin et al.}\text{[82]}\text{ found that with the increase of laser energy density, the grains coarsened and changed from columnar into equiaxed grains. Qin et al.}\text{[82]}\text{ showed that as the laser scanning speed increases, the number of columnar grains growing along the building direction will decrease. It is reported that the formation of columnar grain structure is able to be explained by the epitaxial solidification and the grain growth competition}}\text{[83,84].}
Epitaxial solidification is one special phenomenon, during which the crystallographic orientation depends on that of the crystal grain on the base metal side of the fusion line\textsuperscript{85,86}. The crystals forming at the solid/liquid interface inherit the grain structure and crystalline orientations of the previously solidified layer. Therefore, epitaxial solidification is caused by low undercooling preceding the solidification front due to the repeated local melting and remelting of Zn-based materials, which is the energetically favorable mechanism for the columnar grain growth during LPBF\textsuperscript{87}. On the other hand, the formation of grain structure is decided by the thermal flow direction and solidification rate of metal materials according to solidification theory\textsuperscript{88}. During solidification, the Zn grains may undergo different growth degrees, which depend on the codirectionality degree of the preferred growth directions with the sharp heat gradient\textsuperscript{89}. As shown in Figure 5A, a single track of laser scanning was investigated. In these processing conditions, the growth rate of dendrite/cell along the growth direction $v_{\phi}$ involves the solidification front velocity $v_s$, which is related to the thermal source velocity $v_{sc}$, as described by \textsuperscript{89}:

$$v_{\phi} = v_{sc} \cos \phi = v_{sc} \cos \theta$$  \hspace{1cm} (2)

Where, the $\phi$ represents the angle between the preferred growth direction of Zn grains and unit direction.

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**Figure 4.** (A) The schematic of evaporation fumes and spatters. Reprinted from *Journal of Materials Processing Technology*, 258, Wen P, Jauer L, Voshage M, et al., Densification behavior of pure Zn metal parts produced by selective laser melting for manufacturing biodegradable implants, 128-137, Copyright (2018), with permission from Elsevier\textsuperscript{34}. (B) The evaporation fumes of Zn during LPBF. Reprinted from *Acta Biomaterialia*, 98, Qin Y, Wen P, Guo H, et al., additive manufacturing of biodegradable metals: Current research status and future perspectives, 3-22, Copyright (2019), with permission from Elsevier\textsuperscript{35}. (C) The dynamic X-ray images of liquid-solid powder agglomeration spatter during LPBF. Reprinted from *Additive Manufacturing*, 36, Young Z A, Guo Q, Parab ND, et al., types of spatter and their features and formation mechanisms in laser powder bed fusion additive manufacturing process, Copyright (2020), with permission from Elsevier\textsuperscript{76}.
perpendicular to the front of solidification and the $\theta$ is the angle between and unit direction perpendicular to the front of solidification. According to the Equation 2, unfavorably oriented grains become blocked and stop growing when some growth directions are far away from thermal flow direction during LPBF.

The microstructure of Zn parts of LPBF is displayed in Figure 5B. Due to Zn with hexagonal close packed structure, the preferred grain growth direction is $<0001>$ direction, which shows the highest growth rate\[91\]. It is worth noting that the grains showing in blue within the coarse columnar grains possess different growth orientation angle due to the influence of twinning. It is attributed to a significantly large crystal axis ratio of 1.856 for Zn as compared with an ideal hexagonal crystal (1.732), which easily leads to the occurrence of massive twinning on the (1012) plane\[92\]. With the increase of scanning speed, the columnar grains along the build direction become fine polygonal grains with more random orientation for LPBF-processed Zn matrix, and their average grain width reaches 5.9 $\mu$m. Meanwhile, the number and size of twinning also reduced. The results indicate that the preferred growth directions of favorably oriented grains are well consistent with the direction with the thermal gradient directions, while their adjacent grains misorient at a certain angle in respect of the heat flow direction during rapid solidification. In addition, due to relatively fast solidification of molten liquid in molten pool under the condition of increasing scanning speed, the formation of massive nucleation leads to relatively large density and randomly oriented grains, which weakens texture of LPBF-processed Zn matrix\[93\]. As displayed in Figure 5C, with the increase of scanning speed, texture strength gradually weakened.

Given the fact that LPBF precisely adjusts the microstructure for Zn, the special microstructures for a series of biological Zn-based materials developed by alloying technology are also widely studied. Usually, the
alloying elements including Mg, silver (Ag), and cerium (Ce) with Zn matrix can form second phases\(^3\). During laser melting Zn, the volume and size of the second phases can be reduced in Zn matrix, which is attributed to the characteristics of laser rapid solidification\(^9\). In the molten pool formed by laser irradiation, the highly supercooled melt causes rapid solid-liquid interface movement, which results in obvious deviation from equilibrium at the interface. Although the total free energy of the melt decreases during crystallization, the chemical potential of the minor components in the binary alloy tends to increase\(^9\). In this case, the solute concentration far exceeds the equilibrium solid solution limit, which is called “solute capture”\(^9\). Thus, solidification only involves short-range atom rearrangement at the interface and no long-range diffusion movement, which proceed much more rapidly than solute atomic diffusion. According to the model of solute redistribution during continuous growth with rapid solidification, the coefficient \(z\) of solute distribution at the interface is determined by\(^9\):

\[
Z_v = \left( Z_e + \frac{R_i}{V_d} \right) / \left( 1 + \frac{R_i}{V_d} \right)
\]  

Where, the \(z\), \(R_i\), and \(V_d\) are the equilibrium segregation coefficient, the interface growth rate, and the diffusion rate of solute atom at the interface, respectively.

Based on the Equation 3, the \(z\) is a dynamic dependent variable that changes monotonously from the \(z\) to 1 as the \(R_i\) increases. In other words, the \(R_i\) is directly proportional to the laser scanning velocity during LPBF.

The influence of the scanning velocity on the microstructure of Zn alloys is analyzed during LPBF, as displayed in Figure 6A. Usually, the relatively high scanning rate leads to the rapid solid-liquid interface movement, which causes the obvious deviation of the local equilibrium conditions near the interface\(^9\). In this condition, Al atoms possess insufficient diffusion time and incorporate into the Zn matrix, thereby reducing the segregation of the second phase. With the decrease in scanning speed, the heat accumulation within the molten pool is enhanced and difficult to dissipate, which leads to a reduced cooling rate\(^9\). An extended cooling period is considered to provide improved kinetics qualifications for grain growth, which results in grain coarsening. Meanwhile, Al atoms avoid being engulfed by growing solids and precipitate at the grain boundary. In addition, alloying can improve the random orientation of grains and weaken the texture of LPBF-processed Zn matrix, as displayed in Figure 6B. Obviously, the preferable grain orientation for Zn alloys is weakened, and the texture components of (0001) plane diffuse randomly around.

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**Figure 6.** (A) Cross-sections of the laser powder bed fusion-processed Zn-Al parts obtained at various volume energy densities. Reprinted from *Journal of Alloys and Compounds*, 798, Shuai C, Cheng Y, Yang Y, *et al.*, laser additive manufacturing of Zn-2Al part for bone repair: Formability, microstructure, and properties, 606-615, Copyright (2019), with permission from Elsevier\(^3\). (B) Inverse pole figures and corresponding pole maps for as-build Zn-based parts. All maps are observed along the building direction. Reprinted from *Composites Part B-Engineering*, 216, Yang Y, Yang M, He C, *et al.*, rare earth improves strength and creep resistance of additively manufactured Zn implants, Copyright (2021), with permission from Elsevier\(^79\).

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It is ascribed to that the Ce with high surface activity reduces surface tension of liquid phase in LPBF process and reduces the critical nucleation radius\(^{[100]}\). Meanwhile, the precipitates further hinder the growth of primary grains along one single direction, thereby forming fine grains with random orientations\(^{[79]}\). However, the component content of the second phases is easily changed due to the burning loss of elements caused by evaporation, thereby affecting the microstructure of Zn matrix to a large extent. According to a report of LPBF-processed ZK60, the mass ratio of Zn element decreases from 5.2% in the alloying powders to 4.4% in the as-built part, while the Mg element content rises from 94.0% to 94.4%, which is attributed to the evaporation tendency of Zn element which is higher than that of Mg element\(^{[101]}\). Since Mg has high oxidation tendency, formed oxide film need to be melted by high laser energy input as compared with Zn. In this case, both size and content of precipitates within Zn matrix increase. Therefore, the microstructure composition analysis for LPBF-processed Zn needs to consider the effect of metal elements on evaporation.

3.2. Mechanical properties

The biomedical metal with similar mechanical properties of bone is required, which is favorable to stress stimuli and avoidance of stress shielding\(^{[102]}\). Zn implants as plate or screw offer sufficient mechanical strength for clinical applications. However, Zn scaffolds, especially with high porosity, still show relatively poor mechanical properties as hard tissue repair material\(^{[72]}\). An undoubted fact is that the processing method directly affects the mechanical properties of Zn. As shown in Table 2, the as-cast Zn exhibits relatively poor ultimate tensile strength of 33.6 ± 0.6 MPa and tensile elongation of 1.2 ± 0.3%. Although the ultimate strength and elongation for the hot-rolled Zn reached 153.1 ± 3.2 MPa and 61.4 ± 1.2%, respectively, this method is difficult to customize bone implants with porous structure\(^{[100]}\). In contrast, Zn prepared by LPBF with optimizing process parameters possesses relatively high elongation of 8.1 ± 0.9% and ultimate strength of 132.9 ± 0.7 MPa\(^{[82]}\). Despite that the mechanical properties of the LPBF-processed samples are affected by sample size and defects, it still shows other excellent properties\(^{[104]}\). In addition, the porous Zn scaffolds fabricated by LPBF have also great practical potential in the bone repair. For instance, Montani et al.\(^{[83]}\) processed porous Zn using LPBF method in 2017 and found laser melted Zn presented more superior mechanical properties than as-cast and wrought Zn material because of reduced grain size. According to the Hall-Petch law, fine grains obtained by laser rapid solidification are able to enhance the resistance near the grain boundary, which leads to the accumulation of extensive dislocations and the strength improvement\(^{[105]}\). Meanwhile, grains with varied orientation against the original one can accommodate more deformation strain under tensile loading, which improves the ductility. To further understand the fracture mechanism, laser melted Zn exhibited a typical characteristic of cleavage steps surrounding the tearing ridge. With the increase of scanning speed, the cleavage steps become small and deep. Cleavage facets arrayed in a certain direction are not found, and the grains tend to be ruptured in a transgranular manner.

Alloying treatment is usually adopted to enhance the mechanical properties of Zn implants\(^{[113-115]}\). Zn-Mg alloy is the most studied in Zn-based medical alloys due to their favorable biocompatibility. For instance, the LPBF-fabricated Zn-3Mg parts exhibit significantly enhanced ultimate strength of 222.3 ± 8.2 MPa, which is attributed to the grain refinement strengthening, solid solution strengthening, and secondary phase strengthening caused

| Material     | Metallurgy | Grain size | Yield strength | Ultimate strength | Elongation |
|--------------|------------|------------|----------------|-------------------|------------|
|              |            | \(\mu m\)  | MPa            | MPa               | %          |
| Zn           | Casting    | /          | 29.3           | 33.6              | 1.2        |
| Zn           | Hot rolled | /          | 84.2           | 153.1             | 61.4       |
| Zn           | LPBF       | 5.9        | 110.3          | 132.9             | 8.1        |
| Zn-Al        | LPBF       | 2.21       | 141.7          | 192.2             | 11.7       |
| Zn-Mg        | LPBF       | 5.2        | 152.4          | 222.3             | 7.2        |
| Zn-Mg        | Casting    | 65         | 112            | 120               | 0.6        |
| Zn-Ce        | LPBF       | 3.9        | 180.6          | 247.4             | 7.5        |
| Zn-Li        | Hot rolled | 5.9        | 363.7          | 405.3             | 4.0        |
| Zn-We43      | LPBF       | 5.6        | 298.5          | 335.4             | 8.0        |
| Zn-RGO       | LPBF       | 3.2        | 142.9          | 182.1             | 14.1       |
| Human bone   | /          | /          | 124 – 174      | 150 – 180         | 1.4-3.1    |
by alloying treatment with Mg. Introducing Ag into Zn by LPBF also improves the mechanical strength of Zn matrix. Alloying with Ag can form the constitutional undercooling in front of the moving solid-liquid interface, which leads to more nucleation events and the grain refinement. On the other hand, abundant precipitates (AgZn) act as active nucleation sites to further refine the Zn grains, thereby effectively hindering dislocation movement and plastic deformation. Besides, Shuai et al. introduced Al and Sn into porous Zn scaffolds prepared by LPBF methods, and the additives effectively enhance the mechanical strength of Zn scaffolds. In detail, the Al phase nucleated primarily during cooling and caused the rapid precipitation of Zn, and then, the Zn-enriched phase and Sn phase could form rod-like eutectic structure of Zn-Al-Sn phase. In this case, the rod-like eutectic could block dislocation motion and result in dislocation pile-up, thereby conducing to the mechanical reinforcement. Besides, hot-rolled Zn-Li alloy even exhibits an extremely high tensile strength of 405.3 MPa.

REs are also used to improve the mechanical properties of Zn. Compared with other alloying elements, REs have better fine grain effect. It is reported that the nanocrystalline precipitates in Zn matrix generate a remarkable back stress for the bow dislocations around the shear resistant precipitates during stretching, thereby hindering dislocation movement. More significantly, the solid solution of REs in Zn matrix leads to massive edge distortion and lattice dislocation, which further increases the resistance of dislocation movement. As a result, the yield strength, ultimate strength, and elongation for Zn-Ce parts considerably enhance to 180.6 ± 7.1 MPa, 247.4 ± 7.2 MPa, and 7.5%, respectively. Besides, the interaction of metal matrix and multiple alloying elements can also effectively improve mechanical properties, thereby maintaining the initial mechanical stability and long-term bone osseointegration during repairing bone defects. Alloying with WE43 can produce complex intermetallic compounds with Zn porous scaffolds, such as Mg2Zn11, YZn6, and NdZn5, which induce a strong effect of grain refinement. In this case, the hardness of Zn-xWE43 (x = 0, 2, 5, and 8 wt.%) gradually increases from 42 ± 3 to 169 ± 8 HV, and the tensile strength is enhanced to 335.4 ± 10 MPa. However, the elongation gradually decreases due to the increase of precipitate content. Notably, REs can not only improve the mechanical strength of Zn matrix but also enhance the creep resistance at human temperature. In this case, stacking fault energy of Zn is reduced, which leads to the decrease of the critical resolved shear stress and the improvement of lattice symmetry in Zn matrix, and then benefits the activation of non-basal slip including sessile pyramidal slip.

Nano reinforcements, including nanoparticle, nanorod, and nanosheet, exhibit great potential to enhance the mechanical properties of metal-based composites, because of their high specific strength and elastic modulus. The possible strengthening mechanism mainly includes grain refinement, load transfer effect, Orowan strengthening, as well as thermal mismatch strengthening. Among them, load transfer effect is a primary strengthening factor since the load is easily transferred from the metal matrix to reinforcements through the interfacial shear stress. Under this condition, nano reinforcements can consume massive fracture energy and prevent the crack propagation, thereby achieving enhancement effect. Grain refinement, as another major strengthening factor, is attributed to the heterogeneous nucleation effect of nano reinforcements. Usually, the nucleation of new grains at the solidification frontier requires numerous nucleation sites and a favorable energy condition. Nano reinforcements with high melting point lead to a significantly enhancement of supercooling at the solid/liquid interface, which provides an energetically favorable condition. Meanwhile, the reinforcements can act as low-energy barrier heterogeneous nucleation sites ahead of the solidification front, thereby inducing the random growth of fine grains. Thermal mismatch expansion differences between the matrix and reinforcements are also caused by massive lattice distortion at the interface to realize the enhancement of mechanical properties. Nevertheless, Orowan strengthening only takes effect in the composites with uniformly distributed nanoparticles. The nano reinforcements within the grain are able to accumulate, pin down, and form dislocation loops, there generating a back stress that hindered dislocation propagation. For example, reduced graphene oxide (RGO) is used to prepare Zn-based scaffolds. The results show that RGO in Zn matrix remarkably enhances the strength to 182 MPa. Besides, nano silicon carbide was incorporated into Zn matrix through LPBF, which results in high compressive yield strength of 121.8 ± 5.3 MPa.

Obviously, both the introduction of alloy elements and nano reinforcements can effectively improve the mechanical strength of Zn implants. However, alloying treatment may also give rise biological problems. Therefore, it is necessary to choose some alloy elements with high tolerance to human body. In addition, how nano reinforcements are absorbed by human body during the degradation of Zn is another unsolved problem. Some literature reported that carbon nanomaterials were able to achieve complete metabolism in body fluid by human myeloperoxidase, eosinophil peroxidase, and xanthine oxidase, and even be taken up by cells due to its nanoscale structure. The introduction of bioactive ceramics such as hydroxyapatite and bioactive glass as reinforcing
phase may be a future choice. Bioactive ceramics can simultaneously improve the mechanical and biological performance of biodegradable metals. Nevertheless, to the best of our knowledge, studies regarding LPBF of Zn-based composites containing bioactive ceramics are currently unavailable. Besides, the fatigue behavior of degradable Zn implants is also very important because the implants in the load-bearing parts need to bear cyclic loads in human body. Li et al.\textsuperscript{[144,145]} showed that LPBF-processed porous Zn shows higher fatigue strength than porous Mg alloy under similar structural. The surface roughness and the micropores in the LPBF-processed Zn parts may be used as the nucleation site of the crack. The forming defects can be used as the starting point of the crack and to shorten its fatigue life. The biodegradation behavior will undoubtedly reduce the fatigue life of porous biodegradable metal. However, it was proven that the fatigue life of LPBF-processed porous Zn is better than that tested in air, which may be due to the good combination between the formed degradation products and Zn matrix.

4. Biodegradation behavior

Usually, bone implants are required a mechanical support with at least 3 months and preferably completed absorption within 2 years\textsuperscript{[136,137]}. At present, the degradation behavior of Zn has been reported in a large number of literatures\textsuperscript{[138]}. Its degradation is closely related to microstructure, chemical composition, and porous structure. Li et al.\textsuperscript{[139]} studied the degradation behavior of porous Zn scaffolds fabricated by LPBF. The results showed that their degradation rate was moderate, which lost 7.8\% and 3.6\% of volume after dynamic and static immersion in simulated body fluid (SBF) for 4 weeks, respectively. Qin et al.\textsuperscript{[142]} prepared bulk pure Zn by LPBF and found that the corrosion rate was lower than that of cast Zn. This is due to fine-grained structure caused by the rapid cooling rate and the passivation effect of corrosion products.

Considering the fine grains and homogeneous microstructure obtained by laser rapid solidification, LPBF-processed Zn indeed presents some unique degradation behavior. Theoretically, grain refinement leads to an increase of grain boundaries, which means high degradation reaction of sample surface. The influence of grain size on corrosion rate \((i_{\text{corr}})\) is described by\textsuperscript{[140]}:

\[
i_{\text{corr}} = L_x + L_y(\bar{d})^{-\frac{1}{2}} \cdot \exp\left(-\frac{9}{8} \cdot \frac{\pi}{A^2}\right)
\]

(4)

Where, both the \(L_x\) and \(L_y\) are constants depending on the material composition. The \(\bar{d}\) and \(A\) are the average grain size and the grain size distribution, respectively. Based on the Equation 4, the decrease of grain size leads to more uniform degradation products, which can easily form a dense layer on the metal surface, thus reducing the degradation rate. The texture also influences the corrosion behavior of metal matrix\textsuperscript{[141]}. When the crystal plane \((0002)\) is the major plane parallel to the surface, the textured AZ31 samples show superior corrosion resistance\textsuperscript{[142]}. Similar results are found in the extruded AZ31 samples with preferred grain orientation\textsuperscript{[143]}. Therefore, a strong texture with a preferred growth direction \((0001)\) presents on laser melted Zn samples, which can cause preferential corrosion for other growth directions. In this case, heterogeneous corrosion formation can lead to the increase of corrosion rate.

The elemental composition and precipitates also influence the degradation of Zn implants. The influence of alloying elements on the degradation rate in LPBF-processed Zn is mainly attributed to two aspects, including the grain size and the galvanic corrosion between the precipitated second phase and matrix\textsuperscript{[144,145]}. The fine-grained structure may cause a decreased corrosion rate due to the formation of corrosion products in the passivation environment, and the specific situation is related to the passivation properties of metal surface\textsuperscript{[146]}. For example, Yang et al.\textsuperscript{[33]} processed Zn-Mg implant and found that Mg element could enhance the anti-corrosion ability of Zn implant. The enhancement of Zn-Mg corrosion resistance was mainly due to the increase in grain boundary density because of grain refinement, thereby enhancing the passivation of the surface film.

It is widely accepted that the secondary phase can act as a galvanic cathode, which accelerates the corrosion rate\textsuperscript{[145]}. The specific effect depends on the amount and the distribution of the secondary phases. Shuai et al.\textsuperscript{[116]} revealed the degradation behavior of LPBF prepared Zn-Al-Sn \((x = 0, 0.5, 1, 2, 3)\) alloy and found that Zn-Al-3Sn alloy exhibited the highest degradation rate among all the alloys. In general, in Zn-Al alloy, there were only Zn enriched phase and Zn-Al eutectic phase. With the increase of Sn content, the presence of Sn-enriched phase further enhanced the galvanic corrosion in the Zn-Al-Sn alloy. Therefore, the Zn-Al-3Sn alloy has the fastest degradation rate. Yang et al.\textsuperscript{[60]} investigated the degradation behavior of LPBF-processed Zn-Nd alloy. After alloying with REs, the diameter of the capacitive arc and impedance moduli at low frequency gradually increases to maximum, reflecting a high charge transfer resistance. In general, during the corrosion process, the basic Zn chloride with good compactness is easily affected by carbonate ion to form basic Zn carbonate with amorphous state\textsuperscript{[147]}. However, the ion transfer could be effectively cut off by REs, which maintains the stability of basic Zn chloride, thus decreasing corrosion rate\textsuperscript{[148]}. It should be noted that current studies regarding on the degradation behavior of laser melted Zn-based implants are mainly focused on \textit{in vitro} tests. It is well accepted that...
the degradation rate in vivo is slower than that in vitro due to the complex physiological environment. According to some reports, the degradation research implanted into animals can get a more representative scenario to evaluate degradation behaviors for Zn implants prepared by other processes. Different Zn-1X pin (X = Mg, Ca, and Sr, wt.%) are implanted into mouse femora. The results show that the bone around the implants begins to change continuously due to new bone formation and remodel, and the corresponding degradation rates are 0.17, 0.19, and 0.22 mm/year, respectively. The Zn and Zn-xAl (x = 1, 3, and 5 wt%) strips are implanted into the abdominal aorta of adult rats. It is found that the corrosion develops from the surface toward inside, and partial Zn material remains intact after ½ year. On the other hand, additive manufacturing can prepare complex porous structure, which is also the key to affecting its degradation rate. In general, increasing the porosity will accelerate the degradation rate, but will sacrifice its mechanical strength to a certain extent. Therefore, how to find a balance between biomimetic structure, degradation behavior, and mechanical stability is the future research direction.

5. Cytocompatibility

Medical implants need to have good biocompatibility to avoid toxic effects on the host. At present, there are very few literatures reporting the biocompatibility of LPBF-processed porous biodegradable metal, including Zn, Mg, and Fe. The biocompatibility evaluation of LPBF-processed porous biodegradable metals is still at the cellular and in vitro level. It is well accepted that the factors affecting the biocompatibility mainly lie in its chemical properties and degradation products. Zn is the main degradation product. As one necessary element of human body, about 60% of Zn is stored in skeletal muscle of human body, about 30% in skeleton, about 5% in liver and skin, as well as the rest in other important organs. The recommended dietary allowance for Zn is about 8–11 mg/day, which is far low as compared with the median lethal dose value of 27 g/day. Thereby, the composition design of Zn powder for LPBF in the future should meet the requirement of biocompatibility.

For Zn implants prepared by LPBF, it possesses relatively fine grain and strong texture as compared with that obtained by traditional process. Nevertheless, the current studies proved that they showed similar cell biocompatibility. For LPBF-processed porous implants, its advantage is that the porous structure offers channels for nutrient transport and metabolite excretion, and is conducive to the growth of new tissue. On the other hand, the geometry and microstructure of LPBF-processed porous structure are different from conventional bulk materials, resulting in different biodegradation behaviors, which should undoubtedly influence the cell response. Wang et al. reported that large pores of metallic scaffold favor nutrient supply, whereas the small pores are beneficial for cell growth. In this respect, the biocompatibility of LPBF-processed Zn scaffolds can be affected by regulating the pore structure. Up to now, some researchers have performed some preliminary investigations on the impact of geometric design of LPBF-processed degradable Zn on the biological behavior. For example, Li et al. prepared functionally graded porous Zn with precisely controlled topology using LPBF and studied the effects of different pore sizes on the cell behavior of scaffolds. The results showed that a smaller pore size provided a larger strut surface area for cell-surface interactions before cells passed through the pores. In addition, the scaffolds designed of radial direction (i.e., along the x and y axes) also affected cell growth. It was pointed out that the rates of tissue formation increased with the increase of the curvature of porous scaffolds and are faster on concave surfaces than on convex surfaces and planes.

The surface morphology of LPBF-processed porous implants also affects the reaction between implant and host tissue. LPBF-built parts are usually stained with unmelted particles, which will increase the risk of bacterial colonization. Relevant researches showed that the nanosurface topology could induce the osteogenic differentiation of stem cells and promote the adhesion of osteoblasts. Thus, nanosurface topology is a future choice to improve the tissue integration performance of implants in vivo. The conventional surface treatment methods such as sand blasting and chemical erosion are generally used to improve the surface quality of LPBF-processed biodegradable metal. However, it is not able to obtain a uniform and smooth surface inside the scaffolds, which may lead to the difference of degradation in different sites of scaffolds and the premature loss of mechanical integrity. Surface coatings including bioactive ceramics and biopolymers have been widely used to regulate the biological function of bulk degradable metals. Furthermore, the coatings have been studied with the purposes of improving degradable metal porous materials. Furthermore, the coatings have been studied with the purposes of improving degradable metal porous materials. For example, Zhuang et al. designed a new porous Zn scaffolds with Ca-P coating and found that it effectively promoted osteogenic differentiation and calcium deposition of rabbit BMSCs in vitro, and new bone formation around the scaffold in vivo. However, how to form a uniform coating inside porous scaffolds is still a challenge.

In addition, Zn belongs to inorganic antibacterial materials. Therefore, degradable Zn implants exhibited a good antibacterial property. Bacterial
Zhou, et al. 

inhibition efficiency for laser processed Zn implant reaches 34.28% \((79)\). In fact, the released Zn ions can be adsorbed to the bacteria surface by Coulomb force, which interferes with cell wall synthesis, thus leading to the loss of cell wall integrity \((79)\). On the other hand, once Zn ions penetrate the cell wall, it can replace the cation position of the cell membrane, thereby destroying the cell membrane metabolism and structure \((172)\). However, the antibacterial effect of Zn ion is limited. Till now, Cu, Ag, and Ce that possessed powerful antibacterial effect were added into Zn-based implants \((79,173,174)\). One concern is that the addition of these alloying elements may reduce the biocompatibility of Zn implants to a certain extent, since they have lower tolerance than Zn in the human body. Furthermore, the reports on the LPBF of antibacterial Zn-based implants are in the form of multiple powder mixtures, such as Zn powder and Nd powder. It is difficult to ensure the microstructure uniformity of as-built parts. From this point of view, it is necessary to develop special antibacterial Zn-based functional powder for LPBF.

6. Remarks and perspectives

LPBF is regarded as an ideal process for the fabrication of Zn implants, since it can precisely control the inner porous structure and outer complex shape. The resulting formation quality and properties including mechanical and degradation of LPBF-processed Zn implants are decided by the powder properties, processing, design, and chemical component. Although great progress has been achieved in understanding and optimizing the LPBF-processed Zn in the last several years, the current development is still in the infancy stage as compared with other biomedical metal. Therefore, to realize the clinical application of LPBF-processed Zn, a considerable amount of researches are necessarily considered in the future.

(1) The implants require the metal materials to provide appropriate mechanical properties, suitable corrosion rate and excellent biocompatibility, as well as biological activity in human body. Usually, the mechanical and degradable performances are strongly decided by the microstructure, which results from alloy composition design, element selection, and process parameters. At present, the Zn powder used for LPBF is developed based on the traditional manufacturing process. During LPBF of Zn-based metal, the chemical composition usually varies due to the metal evaporation. As a result, the chemical composition of the final parts may deviate far from the composition of the initial powder, which may have an important impact on its microstructure and properties. According to the requirements of clinical performance, the development of specialized Zn-based powder for LPBF is an urgent issue to be addressed.

(2) Although the microstructure and formation quality of Zn metals have been preliminarily studied, the processing defects related to LPBF such as pore formation, crack, oxidation, and residual stress should be further studied. Effect of multi-alloy elements in Zn matrix on the formation quality also deserves attention. A fact is that LPBF of Zn is a very complex non-equilibrium metallurgical process, which involves physical processes such as melting, evaporation, solidification, and solid-state phase transformation. The composition, structure, and properties of materials have changed dramatically. From this aspect, it is still necessary to clarify the basic theory of laser manufacturing Zn metal and realize the additive manufacturing process with high reliability, high precision, and high flexibility.

(3) Porous scaffolds possess high specific surface area, which leads to relatively high degradation rate compared with the bulk samples. In this case, the gradient structure, topology structure, material design, or special surface modification of LPBF-prepared Zn porous scaffolds need to be studied, aiming to keep mechanical integrity during reconstruction. In addition, Zn-based implants with interconnected pores provide necessary growth space for ingrowth of tissue cells. Considering this factor, the effect of porous scaffolds with different structures on biocompatibility deserves attention. Great numbers of in vitro studies for LPBF-fabricated Zn-based implants have highlighted promising result. However, the assessment and mechanism of the biological interactions between released Zn ions and other ions still lack related in vivo studies. Therefore, comprehensive tests using various animal models and implant locations should be performed in the future work.

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Conflict of interest

The authors declare no known conflicts of interest.
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