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Effects of magnesium on microstructure, properties and degradation behaviors of zinc-based alloys prepared by selective laser melting

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Abstract
Selective laser melting (SLM) technology was employed to manufacture Zn–3%Mg alloy and the effects of the addition of Mg elements on the density, microstructure, mechanical property and corrosion behavior of Zn–based alloy additively manufactured parts was investigated. Experiment results demonstrate that the density of pure Zn-based additively manufactured parts under optimal parameters can be up to 96.7%. With the same parameters, Zn–3Mg alloy was prepared by SLM additive manufacturing technology to obtain additively manufactured parts of Zn–3Mg alloy with the density of 96.0%. Compared with pure Zn, the average grain size in horizontal sections of additively manufactured parts added with 3 wt% Mg reduces from about 21.1 μm to about 2.1 μm and columnar crystals in vertical sections are transformed into equiaxed crystals. The microhardness of Zn–3Mg alloy is 2.6 times higher than that of pure Zn and tensile strengths in both the horizontal and vertical directions of Zn–3Mg alloy are twice as high as that of pure Zn. Moreover, the yield strength of Zn–3Mg alloy under compressive load is more than three times higher than that of pure Zn. After immersing pure Zn and Zn–3Mg alloy in simulated body fluid (SBF) for 7 days, their corrosion rates tend to be stable, i.e. about 0.13 and 0.09 mm-year⁻¹ respectively, that is, the corrosion rate of Zn–3Mg alloy is about 70% that of pure Zn.

1. Introduction
A gradual transformation from inert metal to degradable metal witnesses the development of medical metal implant materials [1]. Medical degradable metal should have good biocompatibility, appropriate biodegradation rate and sufficient mechanical properties [2]. Biodegradable metal mainly includes pure magnesium (Mg) and Mg-based alloys, pure ferrum (Fe) and Fe-based alloys, pure zinc (Zn) and Zn-based alloys [3]. It has been found that Mg alloys have good biocompatibility and mechanical properties, but their degradation rate is very high [4–6]. Fe-based alloys show high mechanical properties, but their degradation rate is very low and ferromagnetism affects the use of some medical imaging equipment [7, 8].

The standard corrosion potential of Zn is −0.8 V, which is between Fe (−0.4 V) and Mg (−2.4 V) [2, 9], and Zn as an essential element for human body [10]. Therefore, Zn-based alloy is medical biodegradable metal with great development potential [11–18]. Bolz et al (2001) [19] first proposed that Zn was a potential medical degradable implant material in a patent. Since then, researchers have carried out many studies on degradation behaviors of Zn and Zn-based alloys. Vojtech et al (2011) [20] first conducted biodegradability tests on Zn–Mg and Zn–Al–Cu alloys in simulated body fluid (SBF). Their test results have shown that the corrosion rates of Zn–Mg and Zn–Al–Cu alloys are 50 and 220 mm-year⁻¹ respectively. That is to say, Zn-based alloy shows better corrosion resistance in SBF. Yao et al (2014) [21] studied corrosion resistance of as-cast Zn–xMg alloys (x = 1, 2, 3 and 5 wt%) in NaCl solution and found that the corrosion current density of Zn–3Mg alloy was about 34% that of pure Zn.

Pure Zn is far behind the requirements of medical metal implant materials, especially in orthopedic applications, due to its poor mechanical properties. The tensile strength of as-cast pure Zn is about 20 MPa [22]. Alloying is an important method to improve mechanical properties of Zn. Therefore, the combination of Zn with known biocompatible elements or elements necessary for human function (e.g. Mg [11, 12, 21, 23, 24],

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calcium [11, 24], copper [25], strontium [11], Fe [24], silver [26], lithium [27] and manganese [28]) is an ideal method to improve mechanical properties of Zn-based alloys [24]. Among them, as Mg is a kind of biodegradable metal that has been studied by many researchers, Zn–Mg alloy has attracted special attention from researchers. Methods used by researchers to prepare Zn–Mg alloys include hot extrusion [12, 25], casting [11, 21], and selective laser melting (SLM) [23], etc.

Zheng et al. [11] prepared the Zn–1Mg alloy by casting process. The tensile test results demonstrate that the yield strength, ultimate tensile strength and elongation of as-cast pure Zn are low, i.e. 10.14 ± 2.32 MPa, 18.25 ± 2.99 MPa and 0.32 ± 0.08%, respectively. After adding Mg, the yield strength, tensile strength and elongation of the as-cast Zn–1Mg binary alloy increase significantly to 127.98 ± 10.72 MPa, 184.84 ± 20.91 MPa and 1.82 ± 0.23%, respectively. Yang et al. (2020) [24] prepared the Zn–Mg binary alloy by hot extrusion process. The tensile test results illustrate that pure Zn can be strengthened by Mg. With the increase of Mg content, the strength of pure Zn increases gradually, while the ductility decreases. Kubasek et al. (2016) [12] prepared Zn–xMg alloy (x = 0, 0.8 and 1.6 wt%) with different Mg contents by hot extrusion process and explored their mechanical properties. The results show that the microhardness, compressive yield strength and tensile strength increase from 44 HV, 120 MPa and 80 MPa of pure Zn to 97 HV, 380 MPa and 367 MPa of Zn–1.6 Mg alloy, respectively, with the rise of Mg content.

A combination of SLM with biodegradable metal is considered to bring revolutionary changes in implant development and manufacturing, especially for implants with complex geometry or customized design [29, 30]. Montani et al. [31] published the first paper on the preparation of pure Zn by SLM. The results show that pure Zn has high porosity because of its low boiling point, and the highest density is only 88%. Subsequently, the research team found that samples with a density higher than 98% were collected through SLM experiment on Zn in an open environment and the removal of Zn vapor with auxiliary purge flow [32]. Wen et al. [33] designed a gas circulation system for SLM equipment, which was an effective method to suppress the interference of Zn vapor and stabilize the SLM process of Zn in a closed processing environment. Wen et al. (2018) [9] prepared additively manufactured parts of pure Zn by SLM, with the tensile strength of about 134 MPa higher than those of pure Zn by casting and hot extrusion. Yang et al. (2018) [23] prepared Zn–xMg alloy (x = 0, 1, 2, 3 and 4 wt%) with different Mg contents by SLM and found that the tensile strength of Zn–3Mg alloy reaches the highest 220 MPa when the Mg content was 3 wt%. Furthermore, they carried out immersion corrosion tests on Zn–xMg alloy (x = 1, 2, 3 and 4 wt%) prepared by SLM. Their test results show that the degradation rate of pure Zn is about 0.18 ± 0.03 mm year⁻¹, while that of the Zn–3Mg alloy is only about 0.10 ± 0.04 mm year⁻¹. Yang et al. (2021) [34] prepared Zn-x CE alloy (x = 1, 2, 3 wt%) by alloying rare earth element cerium (CE) with Zn through SLM. The results show that the addition of CE effectively blocks the grain growth and leads to the formation of CeZn₃ intermetallic compound, so as to improve the mechanical strength through grain refinement and precipitation strengthening. Due to the synergistic antibacterial effect of released CE and Zn ions, Zn CE showed good antibacterial efficiency, and the bacterial inhibition rate was 81.36%, while the bacterial inhibition rate of pure zinc was only 34.28%. Zn CE also showed good blood compatibility and no obvious cytotoxicity. Yang et al. (2021) [35] also prepared Zn-x RGO alloy (x = 0.1, 0.2, 0.3 wt%) by alloying reduced graphene oxide (RGO) with Zn through SLM. The results show that the uniformly dispersed RGO improves the strength and ductility of zinc scaffolds at the same time, the incorporated RGO improves the cell behavior of Zn scaffolds, and RGO also improves the corrosion rate of zinc due to grain refinement and micro current effect.

The above studies indicate that Zn–3Mg alloy prepared by SLM is a potential material for degradable medical implants [9, 23, 33]. However, its comprehensive mechanical properties are still too poor, and the control of degradation rate and degradation mechanism have not been fully studied, which seriously hinders the promotion and application of zinc alloy in the biomedical field. In the process of material preparation, multiple alloying is used to obtain materials with excellent comprehensive properties. In the existing reports, zinc-based alloy is at most ternary alloying, and its mechanical properties and corrosion behavior need to be further improved. In this context, the authors expect to further improve the mechanical performance and obtain a moderate degradation rate of zinc alloy by multiple alloying (four, five, six element alloying etc.) of the SLM manufactured Zn-3Mg alloy. Therefore, the SLM additive manufacturing of Zn-3Mg alloy was firstly carried out, and its mechanical properties and corrosion behavior were systematically characterized. The results of this paper lay a foundation for the subsequent research, and provide data support for a full understanding of the relationship between the microstructure, mechanical properties and corrosion behavior of Zn–Mg alloy.

2. Materials and methods

2.1. Materials

In this experiment, we used the spherical pure Zn powder with an average particle size d₅₀ of 19 μm prepared by nitrogen gas-atomization technology. The particle size of powder ranged from 10 to 53 μm. Its morphology
under a scanning electron microscope (SEM) is shown in figure 1(a) and its particle size distribution in figure 1(b). Energy dispersive spectrometry (EDS) results are demonstrated in table 1. Moreover, 3 wt% Mg powder (The particle size of powder ranged from 10 to 46 μm) was added into Zn powder, and then the mixed powder was evenly mixed by a ball mill at a rotating speed of 260 rpm for 4 h, thus obtaining the Zn–Mg powder. SEM morphology and element distribution test results of the obtained powder are shown in figure 2. A ZAMAK3 Zn alloy plate with a thickness of 25 mm was used as a substrate that was polished to be flat with sandpaper before SLM and then cleaned with ethanol.

| Table 1. EDS analysis results of pure Zn powder (wt%). |
|---------------------------------|-------|
| Element | Zn   |
| Point 1 | 100  |
| Point 2 | 100  |
| Point 3 | 100  |

2.2. SLM system
JG-SLM260 SLM equipment equipped with a single-cylinder and unidirectional quantitative powder storage and feeding system was used in this experiment and the thickness of powder layers ranged from 0.02 to 0.10 mm. The laser source of this equipment was from a 500 W single-mode continuous wave (CW) fiber laser with a wavelength of 1.07 μm, focal diameter of 50 μm, focal length of 130 mm and maximum laser scanning speed of 7,000 mm s⁻¹. Figure 3 is the schematic diagram of SLM process.
2.3. Methods

2.3.1. Orthogonal test

To explore the impact of process parameters, a SLM orthogonal test scheme with three factors and three levels was designed. The factors include hatch spacing (μm), laser power (W) and scanning speed (mm/s), as shown in Table 2. The parameter range of orthogonal experiment in this study is determined based on a large number of process parameter exploration experiments previously. In SLM orthogonal test, the layer thickness \( t \) was constant at 20 μm, and the angle between the scanning directions in two adjacent layers was 67°. The schematics of the laser scan trajectory have been added in Figure 3. This scanning trajectory can ensure that the laser scanning path of each layer is different from that of the adjacent layers, which can reduce the anisotropic transfer of energy to the sample as much as possible. The volumetric energy density \( E_v \) is calculated in equation (1):

\[
E_v = \frac{P}{(v \cdot t \cdot H_s)}
\]

where, \( P \), \( t \), \( H_s \) and \( V \) represent the laser power (W), layer thickness (mm), hatch spacing (mm) and scanning speed (mm/s), respectively.

2.3.2. Measurement of relative density

In this study, density \( \rho_t \) was measured by the Archimedes’ method. Given the density of water, the volume was obtained by two measurements with a balance. The specific measurement method is described as follows: a sample hanging in the water by a filament is weighed to obtain \( m_1 \) (buoyant weight). After taking the sample out of water and carefully wiping out excess droplets on the surface with a wet towel, the saturated weight in air \( m_2 \) (wet weight) was measured. The weight after drying is \( m_3 \) (dry weight) and the density of water at that temperature is \( \rho_0 \). Assuming that the volume of an object is \( V \) and the theoretical density of the sample is \( \rho_t \), equations (2) and (3) are derived according to Archimedes’ law.

\[
\rho_0 g V = (m_2 - m_1) g
\]

Table 2. Orthogonal test results and corresponding volumetric energy density, relative density and microhardness.

| No. | Orthogonal design | Laser power (W) | Scanning speed (mm•s\(^{-1}\)) | Hatch spacing (μm) | Volumetric energy density \( E_v \) (J•mm\(^{-3}\)) | Relative density \( \rho_t \) (%) | Microhardness (HV) |
|-----|------------------|----------------|-------------------------------|-------------------|-------------------------------------|------------------|--------------|
| 1#  | 1 1 1            | 100            | 1200                          | 25                | 166.67                              | 92.3             | 38.03        |
| 2#  | 1 2 2            | 100            | 1300                          | 35                | 109.89                              | 94.2             | 40.29        |
| 3#  | 1 3 3            | 100            | 1400                          | 45                | 79.37                               | 95.5             | 41.48        |
| 4#  | 2 1 2            | 110            | 1200                          | 35                | 130.95                              | 95.3             | 40.40        |
| 5#  | 2 2 3            | 110            | 1300                          | 45                | 94.14                               | 94.4             | 39.72        |
| 6#  | 2 3 1            | 110            | 1400                          | 25                | 157.14                              | 95.9             | 43.03        |
| 7#  | 3 1 3            | 120            | 1200                          | 45                | 111.11                              | 93.0             | 40.26        |
| 8#  | 3 2 1            | 120            | 1300                          | 25                | 184.62                              | 95.8             | 41.84        |
| 9#  | 3 3 2            | 120            | 1400                          | 35                | 122.45                              | 96.7             | 43.78        |
The bulk density is calculated in equation (4):

\[ V = \frac{(m_2 - m_1)}{\rho_0} \]  

The density of the sample is calculated in equation (5):

\[ \rho = \frac{\rho_0 m_3}{(m_2 - m_1)} \]  

\[ \rho_t = \rho / \rho_i \]  

2.3.3. Microstructure

The SLM sample was inlaid, ground and polished, and then corroded with nitric acid alcohol (4 wt%) for 10 s. Its microstructure was observed and composition analyzed by combining with SEM and EDS. Phase compositions were analyzed by a Bruker DBADVANCE X-ray diffractometer (XRD) at the scanning rate of 8° min⁻¹ and the scanning angle of 20°–90°. The commercial software MDI Jade was used to process the XRD test results, and the standard PDF card in MDI Jade was used to identify the x-ray peaks. Moreover, the electron backscatter diffraction (EBSD) analysis was performed on the grain size on cross section of the sample by using an Oxford EBSD system. The samples for EBSD analysis are prepared according to the following process: the samples prepared by SLM are inlaid, ground, polished into a mirror, and finally put into an ion beam thinner for ion thinning to eliminate grain deformation and residual stress in the polishing process. The longitudinal direction is defined as the build direction of the specimen, and the transverse direction is perpendicular to the build direction.

2.3.4. Mechanical properties

To know microhardness, the SLM sample was tested with an HXD-1000TMC/LCD microhardness tester under the load of 50 gf for 15 s. The schematic diagram of measuring position for microhardness test is shown in figure 4. A tensile test was conducted with an Instron universal testing machine at the tensile rate of 0.2 mm min⁻¹. A compression test was carried out with the Instron universal testing machine at the compression speed of 0.4 mm min⁻¹. Figure 5 shows dimensions and schematic diagrams of sampling positions of samples for tensile and compression tests.

2.3.5. Electrochemical test

Electrochemical corrosion behaviors of pure Zn and Zn–3Mg alloy samples prepared by SLM process in SBF (37 °C) were studied in an electrochemical workstation (CHI604E, C19680). A three-electrode system, which used saturated KCl calomel electrode (SCE) as a reference electrode, a platinum plate (1 cm × 1 cm) as a counter electrode (i.e. auxiliary electrode) and pure Zn and Zn–3Mg alloy samples as a working electrode, was adopted in the test. The electrode potentials measured in the test were all relative to the reference electrode. Compositions of electrolyte SBF are listed in table 3. An electrolytic tank with samples was placed in a thermostated water bath which was adjusted to 37 °C and the electrodes were connected to the equipment for measurement.

Potentiodynamic polarization (PDP) test: firstly, the open-circuit corrosion potential (OCP) was tested. After stabilizing the OCP (about 1,800 s), the potential scanning rate was set as 1 mV s⁻¹ and the scanning range was OCP ± 4 V for linear polarization. The curves were fitted by the software and the corrosion potential (Vcorr) and corrosion current (Icorr) of the samples were calculated. The electrochemical corrosion rate of the sample is...
calculated by equation (6) in accordance with ASTM-G114-89.

\[ Cr_i = 0.00327 \times E_W \times I_{corr} / D \] (6)

Where, \( E_W \) represents the mass equivalent of transferred alloy elements; \( E_W = \sum (f_i \times a_i) / n_i \); \( Cr_i \), \( I_{corr} \) and \( D \) indicate the corrosion rate (mm-year\(^{-1}\)), corrosion current density (\( \mu \)A-cm\(^{-2}\)) and density (g cm\(^{-3}\)) of the sample, respectively; \( f_i \) and \( a_i \) denote the mass fraction and atomic mass of the \( i \)th main alloy element, respectively; \( n_i \) means the number of electrons transferred by the \( i \)th main alloy element.

### 2.3.6. Immersion test

The SLM sample was processed into the one with dimensions of 10 mm \( \times \) 10 mm \( \times \) 3 mm according to the standard and then polished to form a bright mirror surface. After that, the sample was ultrasonicated with alcohol in a KH-250DE numerical control ultrasonic cleaner for 20 min and finally dried with a blower for later use. In an immersion test, SBF was used as the immersion medium and the ratio of SBF volume to sample area was 20 mlcm\(^{-2}\). The whole immersion test lasted 28 days at the constant temperature of 37 °C. The variation in pH value of the solution over time was detected during immersion.

The degradation rate of alloy was tested by the weight loss method. The sample weight \( w_0 \) was measured by an electronic balance before immersion. Three samples were taken out every 24 h and immersed into chromic acid (200 g L\( \text{CrO}_3 \) + 10 g L\( \text{AgNO}_3 \)) for 5–10 min after being washed with deionized water for many times, so as to remove corrosion products on the surface. The samples were taken out, cleaned with deionized water and

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**Table 3. Compositions of SBF.**

| Order | Reagent                           | 1000 ml SBF |
|-------|-----------------------------------|-------------|
| 1     | Ultra-pure water                  | 750 ml      |
| 2     | NaCl                              | 7.996 g     |
| 3     | NaHCO\(_3\)                       | 0.350 g     |
| 4     | KCl                               | 0.224 g     |
| 5     | K\(_2\)HPO\(_4\)-3H\(_2\)O\)     | 0.228 g     |
| 6     | MgCl\(_2\)-6H\(_2\)O\)           | 0.305 g     |
| 7     | 1.0 mol L\(^{-1}\) HCl           | 40 ml       |
| 8     | CaCl\(_2\)                        | 0.278 g     |
| 9     | Na\(_2\)SO\(_4\)                 | 0.071 g     |
| 10    | (CH\(_2\)OH\(_3\))\(_2\)CNH\(_2\) | 6.057 g     |
dried, and then \( w_1 \) was determined by an electronic balance. The weight loss of each sample was the difference between \( w_0 \) and \( w_1 \). The average weight loss of three samples was calculated as test results.

The equation based on weight loss method is derived according to ASTM-G31-72.

\[
CR_w = \frac{K W}{D \cdot A \cdot T}
\]

Where, \( CR_w \), \( K \) and \( W \) represent the degradation rate (mm/year), constant \((8.76 \times 10^4)\) and weight loss (g) of the sample, respectively; \( A \), \( T \) and \( D \) indicate the original surface area \((\text{cm}^2)\) of the sample before immersion, immersion time \((\text{h})\) and density \((\text{g cm}^{-3})\) of the sample, respectively.

3. Results

3.1. Relative density

The relative densities and microhardnesses are shown in table 2. There are two methods to measure the relative density of SLM samples, namely Archimedes drainage method and cross-sectional image method. These two methods are used in this experiment. When the cross-sectional image method is used, the relative density is about 99%, which is close to the existing literature reports \([32, 33]\). However, considering that the measurement results of section image method are affected by the selected section, it is not objective. Therefore, the data of Archimedes drainage method are used uniformly. The range analysis was performed on the relative densities in table 3 and the analysis results are shown in table 4. As displayed in table 4, the factors are ranked in a descending order as scanning speed, laser power and hatch spacing according to their significance. Under the conditions of this study, the range analysis results of relative density as an index show that the optimal level of laser power is the second level, the optimal level of scanning speed is the third level, the optimal level of layer thickness is the second level, that is, the optimal parameter combination is the laser power of 110 W, scanning speed of 1400 mm s\(^{-1}\), hatch spacing of 35 \(\mu\)m. This combination does not appear in the orthogonal design table, however, the parameter combination with the highest density \((9 \#)\) among all the parameter combinations in the orthogonal table is selected as the optimization parameter in this study.

Figure 6 illustrates the effect of main SLM parameters on the density. As the laser power increases, the density firstly rises and then reduces. With the increasing hatch spacing, the density firstly increases and then decreases.

![Figure 6. Response of SLM parameters to the density. (a) Scanning speed; (b) Laser power; (c) Hatch spacing.](image)

### Table 4. Range analysis based on orthogonal test results of density.

| Factor Level | Laser power | Scanning speed | Hatch spacing |
|--------------|-------------|----------------|---------------|
| K 1          | 282.00      | 280.60         | 284.00        |
| K 2          | 285.60      | 284.40         | 286.20        |
| K 3          | 285.50      | 288.10         | 282.90        |
| K avg 1      | 94.00       | 93.53          | 94.67         |
| K avg 2      | 95.20       | 94.80          | 95.40         |
| K avg 3      | 95.17       | 96.03          | 94.30         |
| Optimum level | 2           | 3              | 2             |
| R            | 1.193       | 2.497          | 1.104         |
Figure 7(a) is the scatter diagram for variation in density and microhardness of the sample under each parameter in orthogonal test with the volumetric energy density. Figure 7(b) is the scatter diagram for relationship between microhardness and density. Figure 7(a) reveals that the density and microhardness of the sample both firstly increase and then decrease with the rise of volumetric energy density. Figure 7(b) shows that the microhardness of the additively manufactured parts rises with the increase of density on the whole.

3.2. Relative density and microstructure

The relative densities of pure Zn and Zn–3Mg alloy samples processed by SLM were tested by Archimedes’ method and the results are illustrated in table 5. As shown in the table, the densities of pure Zn and Zn–3Mg alloy are 96.7% and 96.0%, respectively.

Figure 8 displays SEM images and EDS results of pure Zn and Zn–3Mg samples. As shown in the figure, Mg elements are mainly present near grain boundaries, while a few Mg is found in grains. By comparing EDS results at points 1, 2 and 3 (grain boundaries) and that at points 4, 5 and 6 (in grains) in figure 8(h), it is found that Mg has a low content of 1.14 ~ 1.48 wt% in grains, while its content at grain boundary is 5.49 ~ 5.86 wt%.

As demonstrated in figure 9, a strong diffraction peak of α-Zn is detected in pure Zn and Zn–3Mg alloy, while the diffraction peak of Mg2Zn11 is also detected in the Zn–3Mg alloy sample. Based on phase diagram of Zn–Mg alloy, the intermetallic compound Mg2Zn11 is precipitated at about 364 °C [36]. Combined with EDS results in figure 9, it can be inferred that additively manufactured parts of Zn–3Mg alloy prepared by SLM show a dual-phase microstructure composed of Mg in Zn solid solution (α-Zn) and intermetallic compound Mg2Zn11.

EBSD results of vertical and horizontal sections of pure Zn and Zn–3Mg alloy are shown in figure 10, which includes inverse pole figures (IPFs). In IPFs, different colors correspond to different orientations of grains. Observation results of horizontal sections suggest that the grain size decreases after adding Mg. The average grain size of pure Zn is 21.1 μm with the standard deviation of 10.05, while that of Zn–3Mg alloy reduces to 2.1 μm with the standard deviation of 0.94 after adding Mg elements, indicating that Mg can refine the grains of Zn.

Figure 9(c) indicates that the pure Zn sample prepared by SLM contains slender columnar crystals along the vertical direction, sample. This is because the temperature gradient in SLM laser forming process and the rapid melting and solidification of metal powder lead to the growth of grains between multiple deposition layers, so the fine columnar grains grow directionally along the construction direction [9]. While such crystals are not found in Zn–3Mg alloy.

Table 5. Relative densities of pure Zn and Zn–3Mg alloy samples with SLM parameters.

| Sample   | m1(Buoyant weight)/g | m2(Wet weight)/g | m3(Dry weight)/g | Relative Density ρt/% |
|----------|----------------------|------------------|------------------|-----------------------|
| Zn       | 0.77                 | 0.90             | 0.90             | 96.7                  |
| Zn–3Mg   | 0.81                 | 0.96             | 0.95             | 96.0                  |
3.3. Mechanical properties

The test results for microhardness are shown in figure 11. The average microhardness of Zn–3 Mg alloy is 115.29 ± 6.06 HV, which is about 2.63 times that of pure Zn (43.79 ± 2.36 HV). The microhardness of Zn–3 Mg alloy fluctuates in a small range, which may be caused by the change of microstructure. Wen et al [9] found that the hardness of high-density pure zinc parts produced by SLM is 42 HV, which is similar to the results of this
Figure 10. EBSD results of pure Zn and Zn–3Mg alloy.

Figure 11. Measurement results of microhardness (a) Pure Zn and Zn–3Mg samples prepared by SLM; (b) Pure Zn and Zn–3Mg samples prepared by SLM as well as as-cast pure Zn and as-cast ZAMAK3 alloy samples.

experiment. Figure 11(b) presents the comparison results of microhardnesses of Zn, Zn–3Mg, as-cast pure Zn and as-cast ZAMAK3 Zn alloys. It can be seen that the microhardness of Zn–3Mg alloy prepared by SLM is higher than that of as-cast Zn alloy, and the microhardness of pure Zn prepared by SLM is also higher than that of as-cast pure Zn. Li et al [11] reported that the microhardness of as cast pure Zn was 38.24 HV and that of as cast Zn–1Mg was 78.26 HV. Compared with casting, the pure zinc and zinc magnesium alloy samples prepared by SLM obtained excellent microhardness.

Tensile stress curves of pure Zn and Zn–3Mg samples prepared by SLM as well as as-cast pure Zn and as-cast ZAMAK3 Zn alloy samples in the horizontal direction are shown in figure 12(a). Tensile stress curves of pure Zn and Zn–3Mg samples prepared by SLM in the vertical direction are displayed in figure 12(b). The average tensile strength of the pure Zn sample prepared by SLM in the horizontal direction is 97.81 ± 0.62 MPa, while that of
the Zn–3Mg sample in the horizontal direction can reach 197.54 ± 5.35 MPa, according to figure 12(a). Furthermore, the average tensile strengths of Zn–3Mg and pure Zn samples in the vertical direction are 84.34 ± 12.05 MPa and 45.58 ± 3.41 MPa, respectively. The average tensile strengths of the Zn–3Mg sample in two directions are twice that of pure Zn. For the Zn–3Mg sample, its average tensile strength in the vertical direction is about half of that in the horizontal direction, showing significant anisotropy.

In addition, it can be also observed from figure 12(a) that the tensile strength of pure Zn prepared by SLM in the horizontal direction is about 50% higher than that of as-cast pure Zn. The tensile strength of Zn–3 Mg alloy prepared by SLM in the horizontal direction is also higher by about 20% than that of as-cast ZAMAK3 Zn alloy.

Figure 13 shows SEM morphologies of SLM samples subject to tensile fracture. Figures 13(a) and (b) demonstrate the fracture morphologies of pure Zn and Zn–3 Mg after tensile fracturing along the horizontal direction. In the two figures, many cleavage surfaces are observed on fracture surfaces, presenting a typical cleavage fracture mode [20, 37]. Compared with fractures of pure Zn, the area of cleavage surfaces in fractures of Zn–3Mg alloy is smaller [38]. Figures 13(c) and (d) show fracture morphologies of pure Zn and Zn–3Mg samples after tensile fracturing along the vertical direction. As shown in the two figures, two fractures along the vertical direction have not only cleavage surfaces (figures 13(c2) and (d2)), but also unfused zones presenting original morphologies of powder (figures 13(c5) and (d5)). The presence of these unfused zones is the main cause for the low tensile strength of SLM samples in the vertical direction.

Since medical implants often bear alternating tension and compression loads in many cases, the compressive strength is also a key performance index to be considered [39, 40]. Figure 14 shows compression test results. In specific, figure 14(a) illustrates the stress—strain curves obtained by vertical compression; figure 14(b) displays yield strength obtained by vertical compression. The two figures suggest that the average yield strengths of pure Zn and Zn–3 Mg alloy compressed vertically are 64.57 ± 6.17 and 249.81 ± 10.99 MPa, respectively. The addition of Mg significantly improves the average yield strength of Zn-based additively manufactured parts. Figure 14(c) demonstrates the stress—strain curves under horizontal compression; figure 14(d) shows the yield strength and compressive strength obtained by horizontal compression. Under horizontal compression, the average yield strengths of pure Zn and Zn–3Mg alloy are 55.80 ± 8.25 and 291.98 ± 36.61 MPa, respectively while the average compressive strengths of them are 120.40 ± 4.93 and 372.86 ± 3.47 MPa, respectively. Compared with pure Zn, the compressive yield strengths along vertical and horizontal directions separately increase by about 285% and 600% after adding 3 wt% Mg, while the compressive strength along the horizontal direction rises by about 260%.

3.4. Electrochemical corrosion

Corrosion behaviors of pure Zn and Zn–3Mg alloy prepared by SLM in SBF at 37 °C are studied by electrochemical corrosion test. Figure 15(a) shows detection results of open circuit voltage of pure Zn and Zn–3 Mg alloy. Figure 15(b) demonstrates PDP curves of pure Zn and Zn–3 Mg alloy in SBF. From the perspective of thermodynamics, the more negative the corrosion potential is, the worse the corrosion resistance of materials is and the greater the tendency of corrosion is [41]. The corrosion potential Ecorr and corrosion current density Icorr of pure Zn and Zn–3Mg alloy obtained by Tafel extrapolation of PDP curves are as follows: Ecorr values of pure Zn and Zn–3 Mg alloy are −1.04 and −1.01 V, while Icorr values of them are 8.15 and 5.31 μAcm−2, respectively. Based on equation (6), the electrochemical corrosion rates Cri of pure Zn and Zn–3Mg alloy separately are 0.13 mm-year−1 and 0.09 mm-year−1. This indicates that in comparison with pure Zn, the SLM sample with 3 wt%
Mg elements added has better corrosion resistance, while the electrochemical corrosion rate \( C_{RI} \) decreases by about 29.5%.

### 3.5. Immersion test

Increase of pH value of SBF is triggered by OH\(^-\) releasing from corrosion reaction of \( M (M = \text{Zn and Mg}) \) [2].

\[
M + 2H_2O \rightarrow M^2+ + H_2 + 2OH^- \tag{8}
\]

Therefore, the change in pH value of immersion solution reflects the amount of corrosion products and corrosion rate. Figure 16(a) shows the change curve of pH value of SBF with time when it is immersed in different materials. As displayed in the figure, after immersion for four weeks, the pH value of SBF immersing in pure Zn and Zn–3Mg alloy prepared by SLM slowly rises from 7.4 to about 8.2, while that of SBF immersing in as-cast pure Zn sample slowly increases from 7.4 to about 8.4. A change curve of pH value of SBF immersing in ZK60 Mg alloy mostly studied is given to facilitate comparison. It can be observed that the pH value of SBF rises rapidly from 7.4 to about 9.5 after immersing in ZK60 Mg alloy for four weeks.

The pH value of SBF immersing in three kinds of Zn-based materials increases at a higher speed compared with SBF immersing in ZK60 Mg alloy sample. Similarly, the pH value of SBF immersing in as-cast Zn-based materials increases at a faster speed compared with SBF immersing in Zn-based materials prepared by SLM. Adding Mg can slightly suppress the increase speed of pH value of SBF immersing in Zn-based materials prepared by SLM, but the difference is minor on the whole. In addition, the increase speed of pH value of SBF slows down after immersing in pure Zn and Zn–3Mg samples prepared by SLM for 14 days, but rises after continuous immersion for 21 days.

The corrosion rate has been quantitatively analyzed by weight loss method and the analysis results are shown in figure 16(b). The figure demonstrates that the corrosion rates of both materials gradually rise with time in the initial stage and then tend to be stable after immersion for 7 days. It can be observed from the figure that the corrosion rate of Zn–3Mg sample is slightly lower than that of pure Zn after immersion after immersion for
more than 7 days, which is consistent with electrochemical test results (figure 15). After the sample was immersed in SBF for 1 week, the corrosion rate of pure Zn is $0.18 \pm 0.02$ mm·year$^{-1}$ and that of Zn–3Mg is $0.16 \pm 0.01$ mm·year$^{-1}$. The research results of Yang et al. [23] show that after immersion in SBF for one week, the corrosion rate of pure Zn is $0.18 \pm 0.03$ mm·year$^{-1}$ and that of Zn–3Mg is $0.10 \pm 0.02$ mm·year$^{-1}$. Therefore, compared with previous studies on biodegradable zinc based alloys, the degradation rate of zinc based alloys is basically the same. Given that the immersion time is 28 days, the corrosion rate of pure Zn is $0.19 \pm 0.02$ mm·year$^{-1}$, while that of the Zn–3Mg sample added with 3 wt% Mg elements reduces to $0.16 \pm 0.02$ mm·year$^{-1}$ after immersion for 28 days. According to the existing studies, magnesium alloys have good biocompatibility and mechanical properties, but the degradation rate is too fast [4–6]. ZK60 is a typical Mg alloy. Therefore, in this test, the as-cast pure Zn and ZK60 Mg alloy are designed as control groups. The surface
macro-morphologies of the samples in SBF after immersion for 28 days were obtained, as shown in figure 17(a).

It can be concluded that a lot of corrosion products are produced on the surface of ZK60 Mg alloy after immersion for 28 days. The corrosion rates obtained by weight loss test are listed in figure 17(b). The corrosion rate of ZK60 Mg alloy is $1.69 \pm 0.04 \text{ mm year}^{-1}$, which is significantly higher than those of pure Zn and Zn-based alloy. Therefore, zinc alloy has higher corrosion resistance than magnesium alloy and an appropriate degradation rate is crucial for biodegradable metal.

Figure 18 shows surface morphologies of pure Zn and Zn–3Mg alloy prepared by SLM after immersion in SBF for different time durations. The observed morphological characteristics are consistent with previous studies on biodegradable zinc based alloys [11, 20]. It can be observed from the figure that some white flocculent precipitates of 5 $\mu$m appear on the surface of pure Zn after immersion for one day (figure 18(c)) and that all precipitates account for about 5%–10% of the total area of visual field. After immersion for one day, a few white particulate precipitates of 2 $\mu$m are found on the surface of Zn–3Mg alloy (figure 18(d)) and they always occupy a very small area in the visual field.

After immersion for 3 days, a large area of white flocculent precipitates (left side of figure 18E1), some large white precipitates up to 7–8 $\mu$m (right side of figure 18E1) and a lot of small white precipitates of 1–2 $\mu$m (middle of figure 18E1, shown as flocculent morphologies after magnification) are observed on the surface of pure Zn. These precipitates account for about 15%–20% of the total area of visual field. After immersion for 3 days, a large number of small white particulate precipitates of 1–2 $\mu$m (figures 18E1 and F2) are observed on the surface of Zn–3Mg alloy and they occupy about 10% in the total area of visual field.
Figure 18. Surface micro-morphologies of pure Zn and Zn–3Mg alloy after immersion in SBF for different time durations.
After immersion for 5 days, a large area of white flocculent precipitates on the surface of pure Zn accounts for about 50% of the total area of visual field. At the same time, white flocculent precipitates up to 5 μm begin to appear on the surface of Zn–3Mg alloy, but they are not connected into pieces (figure 18H2). These precipitates occupy about 20%-30% of the total area of visual field.

After immersing for 7 days, a large area of white flocculent precipitates on the surface of pure Zn occupies about 70%-80% in the total area of visual field. At the same time, white flocculent precipitates on the surface of Zn–3Mg alloy expand (figure 18J2), while they are not connected into pieces but distributed discretely (figure 18J1).

After immersing for 14 days, precipitates on the surface of pure Zn cover the whole visual field (figure 18K1) and expand in a fluffy manner (figure 18K2). At the same time, precipitates on the surface of Zn–3Mg alloy begin to connect into pieces (figure 18L1) and they occupy about 40%-50% in the total area of visual field.

After immersion for 21 days, precipitates on the surface of pure Zn start to cracking, and cracks coalesce and propagate throughout the visual field. At the same time, precipitates on the surface of Zn–3Mg alloy also begin to crack, but cracks do not propagate throughout the visual field. A small number of small cracks are coalesced in local area (figure 18N1) and most of small cracks are discretely distributed (figure 18N2).

After immersion for 28 days, the width of spreading the whole visual field on the surface of pure Zn increases. These cracks have blurry edges and a small number of unobvious flocculent products appear at cracks (figure 18O2). At the same time, cracks of precipitates on the surface of Zn–3Mg alloy propagate throughout the visual field and coalesce. These cracks have clear edges and do not present flocculent products (figure 18P2).

4. Discussions

4.1. Mechanical properties

Biodegradable implants must have sufficient strength during their service. Pure Zn prepared by SLM has poor mechanical properties, and its average tensile strength in the horizontal direction is 97.81 ± 0.62 MPa. Therefore, it cannot meet the requirements of application in bone tissue engineering. After adding 3 wt% Mg elements (Zn–3Mg alloy), its average tensile strength under horizontal tension increases from 97.81 ± 0.62 MPa to 194.39 ± 5.35 MPa. The strengthening mechanism lies in three factors, i.e. fine-grain strengthening, solid solution strengthening and precipitation strengthening. Besides, the small molten pool and rapid cooling of SLM further enhance these strengthening mechanisms.

As shown in figure 19, the average grain size of pure Zn prepared by SLM is 21.1 μm, while that of Zn–3Mg alloy prepared by SLM under the same process conditions is only 2.1 μm. This indicates that adding Mg has a significant effect of grain refinement. The relationship between the number n of dislocations in the pile-ups and the grain size L is expressed in equation (9) [42]:

\[ n = \frac{L(\tau - \tau_0)}{A} \]  

(9)

Where, L, A and \( \tau - \tau_0 \) represent the radius of grains, constant and effective shear stress for dislocation movement, respectively. According to equation (9), the larger the grain size is, the larger the number n of dislocations in the pile-ups is and the greater the stress concentration is, so that it is easier to initiate the dislocation source of adjacent grains. Based on Hall–Petch relationship [43, 44], grain refinement can improve the resistance to dislocation sliding. When the grain size decreases, the grain boundary area increases significantly, thus enhancing the grain boundary’s resistance to dislocation movement and suppressing the stress concentration at grain boundary when the materials are stressed. In this way, the strength of materials is enhanced. Besides, grain refinement also contributes to more tortuous grain boundary. For example, figure 19 shows that the straight columnar grain boundary disappears at the same time of grain refinement, which needs to consume more energy during crack propagation and is conducive to improving the strength.

Mapping results of the Zn–3Mg sample in figures 19(c)–(e) show that after adding Mg elements, part of Mg is dissolved in Zn matrix to increase the lattice dislocation density of Zn matrix. Based on Yang et al [23], Mg is dissolved in Zn grains, resulting in lattice distortion in Zn matrix, which further increases the resistance to sliding and dislocation movement. Therefore, Mg alloying contributes to solid solution strengthening and improves the tensile property of pure Zn.

Based on XRD results in figure 19(f) and Zn–Mg phase diagram in figure 19(g), the intermetallic compound Mg2Zn11 composed of Zn and Zn–Mg is distributed along grain boundaries. Therefore, another reason for the improvement of mechanical properties is the precipitation strengthening brought by eutectic crystals uniformly precipitated along the grain boundary.

In this study, Zn–3Mg alloy prepared by SLM shows excellent mechanical properties and its average tensile strength in the horizontal direction is up to 194.39 ± 5.35 MPa, which is much higher than that of as-cast 3# Zn alloy (160 MPa). Vojtech et al (2011) [20] reported that the tensile strength of as-cast Zn–3Mg alloy was only about 80 MPa. Yang et al [23] discovered that rapid solidification during SLM inhibits the precipitation of Mg.
and expands the solid solution of Mg in Zn matrix, thus producing supersaturated solid solution. Therefore, Zn–3Mg alloy prepared by SLM shows better mechanical properties than as-cast Zn–3Mg alloy and as-cast 3\# Zn alloy.

4.2. Degradation behavior

Figure 20 illustrates simulation diagrams of pure Zn and Zn–3Mg alloy after immersion in SBF for different time durations. Immersion test results suggest that the corrosion of pure Zn and Zn–3Mg alloy in SBF is mainly characterized by the following process: firstly, the sample is put into SBF and its surface fully contacts with SBF, as shown in figure 20(a). Electrons are removed by metal and enter the solution, while $Ca^{2+}$ and $PO_4^{3-}$ in the solution exchange with metal ions, resulting in the deposition of calcium and phosphorus and the formation of a small number of small spherical particles, as displayed in figure 20(b). With the extension of immersion time, particles deposited on the surface gradually increase, and small-size spherical particle deposits gradually grow, as demonstrated in figure 20(c). As immersion continues, particles gradually agglomerate, as shown in figure 20(d).
After further corrosion, deposits gradually expand to cover the whole sample’s surface, and the loose deposited spherical particles turn into a dense layer with a certain thickness, as displayed in figure 20(e). As the immersion time prolongs further, the thick deposition layer breaks due to stress, as illustrated in figure 20(f). The breaking degree is related to the corrosion time. When the corrosion time is short, the layer of corrosion products is thin, and cracks are narrow and shallow; when the corrosion time is long, cracks are wide and deep. In this case, SBF is in contact with the sample again at fractures and cracks to continue the corrosion, as shown in figures 20(g) and (h). With the progress of corrosion, the deposition layer becomes thicker and cracks are wider, so that the deposition layer will be finally separated from the sample’s surface to promote the deposition of calcium and phosphorus in the next step. By repeating the above process, the deposition process from spherical particles to a dense layer to fracturing is completed and biodegradable metal is gradually degraded.

An appropriate degradation rate is the key to biodegradable metal. Erinc et al found that the repair cycle of a hard microstructure was about 3–12 months, so the degradation rate of biodegradable implant should be slower than 0.5 mm·year⁻¹ [46]. Based on the electrochemical test results (figure 15), corrosion rate quantified by weight loss method (figure 17) and surface morphologies of samples after immersion in SBF (figure 18), Mg alloying can improve the corrosion resistance of pure Zn. Yao et al prepared as-cast Zn–Mg alloys with different Mg contents and investigated their corrosion properties [21]. The results demonstrate that adding Mg elements can improve the corrosion resistance of as-cast Zn–Mg alloys. There are three reasons for improving the corrosion resistance of Zn by Mg alloying. Firstly, adding Mg can refine grains of Zn. Ralston et al [47] revealed the relationship between the grain size ($G_s$) and the corrosion rate of metal (equation 10).
\[ I_{corr} = A + B G^e_{\text{corr}}^{-0.5} \]  

(10)

where, \( A \) represents a function of corrosive environment, which is related to the type of electrolyte; \( B \) indicates the constant of the material, which varies according to the compositions. According to equation (10), the smaller the grain size is, the lower the corrosion current is and the better the corrosion resistance of the material is.

Youssef et al. [48] investigated corrosion behaviors of nanocrystalline Zn and electroplated zinc steel, finding that the smaller grain size of nanocrystalline Zn led to the lower corrosion rate. Secondly, compared with pure Zn, Zn–3Mg matrix can release Mg\(^{2+}\) to produce inert Mg hydroxide carbonate by an irreversible reaction.

\[
2\text{Mg}^{2+} + 2\text{OH}^- + \text{CO}_3^{2-} \rightarrow \text{Mg}_2(\text{OH})_2\text{CO}_3
\]

(11)

Hosking et al. [49] reported that the reversible reaction to produce simonkolleite existed in the solution containing chloride.

\[
5\text{ZnO} + 2\text{Cl}^- + 6\text{H}_2\text{O} \leftrightarrow \text{Zn}_3\text{Cl}_4(\text{OH})_6\text{H}_2\text{O} + 2\text{OH}^-
\]

(12)

Therefore, \( \text{OH}^- \) produced by Reaction (12) is continuously consumed by Reaction (11), thus promoting the development of simonkolleite on the surface. Simonkolleite is considered to be more protective than Zn-based minerals (e.g. hydrozincite and Zn carbonate). Thirdly, a ZnO layer is formed on the surface of pure Zn sample, and a MgO layer is formed on Mg rich phases on the surface of Zn–3Mg sample. The band gap of ZnO is 3.2 eV, which is lower than MgO (7.8 eV). The larger the band gap is, the lower the conductivity is. Therefore, the conductivity of MgO is worse than that of ZnO.

5. Conclusions

This study is designed to explore influence rules and mechanisms of SLM parameters (hatch spacing, laser power and scanning speed) and adding 3 wt% Mg elements on the density, microstructure, mechanical property and corrosion property of Zn-based additively manufactured parts. The main conclusions are drawn as follows:

(1) A set of optimal process parameters was obtained by orthogonal test. When the laser power, hatch spacing and scanning speed are 120 W, 35 \( \mu \text{m} \) and 1,400 mm \( \text{s}^{-1} \), respectively, additively manufactured parts of pure Zn has the density up to 96.67\%, tensile strengths in the horizontal and vertical directions of about 97.81 and 45 MPa respectively, and average microhardness of about 43.79 HV. With the same SLM parameters, the density of additively manufactured parts of Zn–3Mg alloy is 95.99\%.

(2) The grain size of Zn–3Mg alloy is smaller than that of pure Zn. After adding 3 wt\% Mg, the average grain size on horizontal sections of additively manufactured parts reduces from about 43.67 \( \mu \text{m} \) to about 2.84 \( \mu \text{m} \). The columnar crystals in the vertical sections are transformed into equiaxed crystals. Mg elements in additively manufactured parts of Zn–3Mg alloy are mainly precipitated at the grain boundary and a few of them are dissolved in Zn matrix. In addition to the diffraction peak of \( \alpha \)-Zn, the intermetallic compound Mg\(_2\)Zn\(_{11}\) is also detected in additively manufactured parts of Zn–3Mg alloy.

(3) Mechanical properties of Zn–3Mg alloy are superior to those of pure Zn. Specifically, the microhardness of Zn–3Mg alloy prepared by SLM is about 2.6 times that of pure Zn, and the tensile strengths in the horizontal and vertical directions are twice those of pure Zn. Under compressive load, the failure strength of Zn–3Mg alloy in the horizontal direction is about 3.3 times that of pure Zn and the yield strength is about 5.2 times. In the vertical direction, pure Zn and Zn–3Mg alloy both do not break, but the yield strength of Zn–3Mg alloy is about 3.9 times that of pure Zn.

(4) The corrosion resistance of Zn–3Mg alloy is better than that of pure Zn. The corrosion rates \( C_{\text{tri}} \) of pure Zn and Zn–3Mg alloy prepared by SLM are 0.1256 and 0.0886 mm·year\(^{-1}\), respectively, so the latter is 70\% of the former. The corrosion rates of pure Zn and Zn–3Mg prepared by SLM tend to be stable after immersion in SBF for about 7 days and slightly fluctuate near 0.19 and 0.16 mm·year\(^{-1}\), respectively.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.
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