Selective Laser Melted Rare Earth Magnesium Alloy with High Corrosion Resistance

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Abstract: Magnesium (Mg) degrades too fast in human body, which limits its orthopedic application. Single-phase Mg-based supersaturated solid solution is expected to possess high corrosion resistance. In this work, rare earth scandium (Sc) was used as alloying element to prepare Mg(Sc) solid solution powder by mechanical alloying (MA) and then shaped into implant using selective laser melting (SLM). MA utilizes powerful mechanical force to introduce numerous lattice defects, which promotes the dissolution of Sc in Mg matrix and forms supersaturated solid solution particles. Subsequently, SLM with fast heating and cooling rate maintains the original supersaturated solid solution structure. Immersion tests revealed that high Sc content significantly enhanced the corrosion resistance of Mg matrix because of the formation of protective corrosion product film, which was also proved by the electrochemical impedance spectroscopy measurements. Thereby, Mg(Sc) alloy showed a relatively low degradation rate of 0.61 mm/year. In addition, cell tests showed that the Mg(Sc) exhibited favorable biocompatibility and was suitable for medical application.

Keywords: Mg alloy; Rare earth; SLM; Degradation behavior; Biocompatibility

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Alloying treatment is commonly used to improve the degradation performance of Mg\textsuperscript{11}. Alloy elements are either dissolved in matrix or precipitated at grain boundary as second phase, which can improve the mechanical properties by means of solution strengthening or precipitation strengthening\textsuperscript{12}. However, the precipitates in Mg matrix usually induce galvanic corrosion due to the potential difference, thereby inevitably deteriorating the degradation behavior\textsuperscript{13}. Assuming that alloy elements can be completely dissolved in Mg matrix to form supersaturated solid solution, it is expected to significantly improve the degradation performance\textsuperscript{14}. However, the solid solubility of most alloy elements in Mg matrix is extremely small, which poses a huge challenge to prepare Mg supersaturated solid solution. Mechanical alloying (MA) is able to prepare supersaturated solid solution through dislocation solute-pumping mechanism\textsuperscript{15}. In detail, the particles are plastically deformed during ball milling due to the heavy collision of the powders and milling balls, which generate a large number lattice distortions and dislocations\textsuperscript{16}. It is known that the solute diffusivity along the dislocations is relatively convenient as compared with that of the inner grain regions without lattice defect\textsuperscript{17}. Therefore, those crystal defects offer suitable diffusion paths for solute atom\textsuperscript{18}. With continuously milling, the dislocations within the particles will be continually forced to glide, which drags the solute atoms existing in the dislocation region. This allows the solute atoms to gradually diffuse into the crystal lattice of the solvent, obtaining solid solution structure.

To obtain final clinical application, the supersaturated solid solution particles should be shaped into parts with specific structure\textsuperscript{19}. Selective laser melting (SLM) is a type of powder bed fusion technique\textsuperscript{20–22}. Meanwhile, it is also a rapid melting/solidification technology, which has great potential in preparing bulk supersaturated solid solution parts. It is considered that laser beam has the characteristics of high-energy density and small action area\textsuperscript{23}. SLM of solid solution powder exhibits a fast heating rate that can fuse the powder into supersaturated melt and then the micro-molten rapidly cools by non-interface heat conduction (\(\times 10^{3} \) K/s), which is much higher than the critical cooling rate required to form supersaturated solid solution\textsuperscript{24–29}. At present, a large number of researchers have reported SLM of Mg alloys and made some substantive progress\textsuperscript{27}.

Basing on above consideration, herein, rare earth element Sc was used as alloying element to firstly prepare Mg(Sc) solid solution powder by MA and then developed into parts using SLM. Sc has a large solid solubility of 24 wt% in \(\alpha\)-Mg at 730°C, but only 1.5 wt% at room temperature\textsuperscript{28}. Thus, MA combined with SLM is expected to obtain Mg(Sc) parts with high content of dissolved Sc. The microstructure feature and degradation performance were studied. Besides, the biocompatibility was also investigated using \textit{in vitro} cell experiment.

2. Materials and methods

2.1. Original materials and MA process

Spherical Mg powder (purity 99.9%, Shandong Weihao Magnesium Powder Ltd., China) and irregular Sc powder (purity 99.99%, Hunan Rare Earth Metal Material Research Institute, China) were used in this work. MA processing was performed utilizing a high-energy planetary mill (Pulverisette 6, Fritsch, Germany). In detail, the powder mixture containing a mass fraction of 25% Sc was placed into a stainless steel grinding bowl, together with stainless steel grinding balls. The anhydrous alcohol (4% mass fraction) was adopted as the process control agent. The ball to powder weight ratio was 20:1, and the rotation speed was fixed at 350 r/min. The whole milling process was carried out under argon atmosphere. To avert the temperature accumulation, an interval of 10 min was adopted after 10 min milling duration.

The phase composition of the milled powders was identified by X‐ray diffractometer (XRD, D8 Advance, Bruker, Germany) with Cu K\(\alpha\) radiation. The scanning rate was determined at 4°/min. High-resolution transmission electron microscopy (HR-TEM, TecnaiG2-20, FEI Company, USA) was further used to characterize Mg(Sc) powder. High-resolution imaging and selected area electron diffraction (SAED) were used to deeply reveal the atomic scale structure of the Mg(Sc) powder. Meanwhile, energy-dispersive spectroscopy (EDS, X-Max 20, Oxford instruments, UK) was adopted to observe the distribution of Sc in Mg matrix.

2.2. Samples preparation and characterization

The consolidated samples of Mg, Mg-Sc, and mMg-Sc (as-milled 40 h) were prepared by a laser forming system. This equipment contained an YLR-500-WC fiber laser, which had a spot size of \(\sim 70 \mu\text{m}\). In addition, an inert gas protection system was adopted to prevent oxidation during processing. A series of preliminary studies were carried out before determining the SLM process parameters. Results indicated that a low laser energy density resulted in the formation of pores and consequent insufficient densification rate due to the high liquid viscosity in the molten pool\textsuperscript{29–31}. In contrast, a high laser energy density led to the evaporation of Mg powder. The main processing parameters were as follows: Laser scanning speed 600 mm/s, laser power 135 W, layer thickness 50 \(\mu\text{m}\), and hatch spacing 50 \(\mu\text{m}\). The previous study reported that the geometry significantly affects the part properties\textsuperscript{32–34}. To eliminate
the influence of shape on properties, all samples in this work were cubic shape.

The microstructure of SLM processed specimens was captured by optical microscopy (OM, DM4700, Leica, Germany), and the phase identification was performed by XRD. Before OM observation, the surfaces of the samples were treated by the standard for metallographic examinations.

2.3. Electrochemical measurements

The samples with a dimension of 1 × 1 × 1 cm³ were prepared for electrochemical tests. Before testing, a wire was soldered to the back of the specimen, and epoxy resin was used for inlay so as to expose only 1 cm² of working surface. Then, the samples were grounded with SiC papers and polished with 0.05 μm water-soluble diamond polishing paste. In this study, the electrochemical tests were performed on an electrochemical workstation (PARSTAT 4000A, Princeton Applied Research, Princeton, NJ, USA), which was equipped with a conventional three-electrode cell system. The saturated calomel electrode was applied as the reference electrode, whereas the platinum electrode and the specimen served as counter electrode and working electrode, respectively. Before the potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) tests, an open circuit potential (OCP) test was performed in the simulated body fluid (SBF, 37°C, pH 7.4) for 20 min to reach a steady value. The potentiodynamic polarization sweep rate was 1 mV/s. The polarization curves were fitted and analyzed by CVview 3.10 software. The AC impedance test frequency scope was 100 k ~ 0.01 Hz, and the amplitude was 10 mV.

2.4. Immersion tests

Immersion tests were carried out in SBF with an exposure ratio of 20 mL/cm². The degradation rate could be estimated by the hydrogen evolution rate. The resin encapsulated sample was placed in an inverted funnel to avoid the escape of hydrogen gas during degradation. Then, a 25 mL burette was inverted above the funnel to record the volume of released hydrogen. After immersion, specimens were washed using a solution containing 20% CrO₃ and 1% AgNO₃ so as to clean the corrosion product. The degradation rates were calculated by the hydrogen evolution volume (P_H) and weight loss (P_W), respectively. The calculation formula was as follows:[35]

\[ P_H = 2.006 \frac{\Delta V}{At} \]

\[ P_W = 2.10 \frac{\Delta W}{At} \]

Where, the ΔV (mL) was the total volume of hydrogen gas generated during the whole immersion time and ΔW (mg) was the weight loss of the specimen. A (cm²) was the surface area and t (day) was the immersion time. The scanning electron microscopy (SEM, EVO 18, Zeiss, Germany) combined with EDS was adopted to observe the degradation surface. The pH was recorded by a pH meter (pH, FE20K, Mettler FiveEasy, Switzerland), and the Mg and Sc ion concentrations were detected by an inductively coupled plasma atomic emission spectrometry (ICP-AES, Optima 7000DV, Perkin-Elmer, Germany).

2.5. In vitro biocompatibility

The BMSC cells were adopted to assess the in vitro cytocompatibility of Sc-containing Mg alloys. Before the experiment, the cells were cultured in Dulbecco’s Modified Eagle’s Medium (DMEM), containing 10% fetal bovine serum, 100 U/mL penicillin, and 100 mg/mL streptomycin. In addition, the samples were soaked in DMEM. The extracts medium was obtained by indirect contact method based on ISO 10993-5:1999. Then, the extracts were diluted to 50% and 10% concentration, respectively. The cells were transferred to a 48-well cell culture plate with a density of 5000 cells/400 μL medium in a well. The culture medium was replaced by 100%, 50%, or 10% extraction. After seeded 1, 4, and 7 days, the fluorescent staining and Cell Counting Kit-8 (CCK-8) assay were employed to assess the cell viability and cells proliferation, respectively. The stained cells were mounted onto glass slides and observed using a fluorescence microscopy (BX60, Olympus, Japan) (n = 1). The absorbance was measured at 450 nm using a spectrophotometer.

2.6. Statistical analysis

In this study, multiple replicate tests were performed for each group of samples and the final experimental results were expressed as mean ± standard deviation. It was regarded to be statistically significant only when P < 0.05.

3. Results and discussion

3.1. Microstructural feature of milled powder

The phase evolution of Mg-25Sc powder was investigated by XRD, with collected spectrum depicted in Figure 1A. Before milling, clear crystalline peaks corresponding to hexagonal close-packed Mg and Sc phases were observed. After milling for 10 and 20 h, the Mg peaks turned relatively broad and weak. Meanwhile, the Sc peaks inclined to disappear. Furthermore, only α-Mg peaks were detected after milling for 40 h. Besides, the diffraction peak of α-Mg(101) evidently shifted to low-angle region, as shown in Figure 1B. It was indicated that Mg(Sc) solid solution powder was prepared after ball milling for 40 h.
Basing on the XRD data, the lattice constants and strain of Mg(Sc) solid solution were calculated using Scherer formula and Williamson-Hall equation\[^{37}\]. The results are shown in Table 1. It could be seen that both the lattice constant and strain increased with increasing milling time. Since the atomic radius of Sc (2.30 Å) was larger than that of Mg (1.60 Å), the solid solution of Sc caused the expansion of Mg unit cell\[^{36}\]. In addition, the grain size of \(\alpha\)-Mg decreased with the extension of milling time, arriving 11.4 nm at 40 h, which suggesting that MA facilitated the formation of nanocrystalline grain.

Transmission electron microscope (TEM) was performed to elucidate the morphology of crystalline phase of Mg-25Sc powder milled for 40 h. The powder morphology is shown in Figure 2A. The SAED ring patterns are displayed in Figure 2B. The phase identification was achieved by comparing the measured distance of SAED pattern with the standard distance in the ICDD database. It could be seen that the diffracted rings were mainly composed of \(\alpha\)-Mg phase. The HR-TEM image of powder is shown in Figure 2C, which revealed the alignment of various lattice planes inside a single region. Furthermore, the selected red square area from Figure 2C was processed through fast Fourier transform (FFT) and inverse FFT. The inverse FFT image, as presented in Figure 2D, showed obvious lattice distortion and dislocation. Comparing with Mg (102) phase, the increased interplanar spacing of Mg (102) suggested the lattice expansion caused by the substitution of Mg atoms by Sc in the hcp-Mg lattice, which was attributed to the lattice expansion and formation single-phase Mg(Sc) solid solution. In addition, the TEM elements mapping of Mg and Sc were conducted to study the elements distribution. As shown in Figure 2E, it could be clearly seen that Sc solute was uniformly distributed on the randomly selected area.

Combining above TEM and XRD results, it was clearly indicated that the Mg(Sc) solid solution was prepared by MA. The corresponding mechanism is schematically illustrated in Figure 3. At early stage, the ductile components of Mg and Sc particles got flattened to platelet shapes, as it undergone plastic deformation by a micro-forging process\[^{38}\]. The powder microstructure was mainly composed of coarse \(\alpha\)-Mg grains and irregular Sc precipitates. With ball milling time increasing, these flattened particles welded together and formed a composite lamellar structure. In addition, the intense ball milling effect resulted in the transient temperature rise in the ball powder collision region. As a consequence, the diffusion rate of atoms in adjacent particles was accelerated. Simultaneously, the Sc particles got gradually diffused into the Mg matrix leading to the formation of Mg(Sc) solid solution. With milling time further extending, the composite powder

| Ball milling time (hours) | Lattice constant (nm) | Crystallite size (nm) | Lattice strain |
|--------------------------|-----------------------|-----------------------|----------------|
|                          | \(a\)                 | \(c\)                 |                |
| 0                        | 0.32096               | 0.52074               | 43.6           |
| 10                       | 0.32132               | 0.52127               | 27.7           |
| 20                       | 0.32197               | 0.52160               | 18.1           |
| 30                       | 0.32236               | 0.52182               | 13.6           |
| 40                       | 0.32259               | 0.52229               | 11.4           |

Figure 1. (A) The XRD patterns of Mg-25Sc powder milled for different time and (B) the enlarged Mg(101) peak.

Table 1. The lattice constant, crystallite size, and lattice strain of Mg-25Sc powder at various ball milling time were calculated by Scherer formula and Williamson-Hall equation.\[^{37}\]
particles had increased hardness and brittleness due to work hardened, resulting in particle fragmentation and got equiaxed dimensions. At end stage, the cold welding and fracture mechanisms eventually reached an equilibrium steady state\(^3\). As a result, the particle size reached a minimum value. Furthermore, a homogeneous microstructure completely composed of nanocrystalline Mg(Sc) solid solution was successfully synthesized.

3.2. Microstructure of SLM processed parts

The OM of the SLM processed Mg, Mg-Sc, and mMg-Sc specimens is shown in Figure 4A-C. It could be clearly seen that a large amounts of Sc particles were presented on the Mg-Sc part. The fusion temperature of Mg and Sc was 924 K and 1814 K, respectively\(^4\). The applied energy density during SLM was sufficient to fully melt the Mg powder, but some of Sc particles melted partially due to the higher melting point. As
for mMg-Sc specimen, a single-phase microstructure was formed. The corresponding XRD patterns, as depicted in Figure 4D, also revealed the same results. In fact, SLM is a rapid prototyping technology using high-energy laser beam as processing heat source and has great potential in the preparation of non-equilibrium alloy. It was believed that the laser has the characteristics of high-energy density and small action area. Laser radiation on the non-equilibrium alloy powder can make the powder skip the crystallization area and melt at a very high heating rate, and then, the micro-molten pool is cooled rapidly through non-interface heat conduction, which is much higher than the critical cooling rate required to form the non-equilibrium alloy[42,43]. Thus, the deposited layer of non-equilibrium alloy structure is obtained. More importantly, SLM can obtain parts through the superposition of deposition layers[44,45]. A number of studies have proven that SLM process is effective in preserving the metastable phase. For instance, Hugo et al.[46] produced fine metastable Al-Fe powders by MA and then processed by SLM. Results showed that metastable Al$_5$Fe$_2$ parts were successfully obtained at suitable laser processing parameters.
3.3. Electrochemical behavior

The OCP test results of Mg, Mg-Sc, and mMg-Sc in SBF are shown in Figure 5A. It was noted that the OCP of three samples gradually reached a saturation value within 20 min, and the OCP of Sc-containing Mg alloys was slightly nobler than that of Mg. In addition, the positive shift rate (ΔE/Δt) of the OCP curve for Mg was relatively higher than that of Sc-containing Mg alloys, suggesting a faster corrosion layer formation on the sample surface. The polarization curves, as displayed in Figure 5B, showed that Mg-Sc alloy exhibited high cathodic current density. It was believed that the large amount of second phase led to the presence of more hydrogen evolution sites at the cathode\(^1\). In the anodic branches, the corrosion current density (i\(_\text{corr}\)) increased slowly with corrosion potential (E\(_\text{corr}\)), and the i\(_\text{corr}\) of Mg grew at the highest rate before breakdown potential (E\(_\text{bd}\)). However, the i\(_\text{corr}\) of Mg was gradually overtaken by that of Mg-Sc alloy after E\(_\text{bd}\). It might be due to the rupture of the local protective film and the re-exposure of the micro-galvanic couples to the corrosive medium, which resulted in an accelerated dissolution rate of the Mg substrate. The detailed corrosion parameters of the polarization curves are listed in Table 2. It was shown that the E\(_\text{corr}\) of Sc-containing Mg alloys was more positive than that of Mg. Meanwhile, mMg-Sc also showed a smaller i\(_\text{corr}\) as compared to Mg and Mg-Sc. In a nutshell, the mMg-Sc alloy with higher E\(_\text{corr}\) as compared to Mg and Mg-Sc had better pitting corrosion resistance.

The Nyquist plots of samples are depicted in Figure 5C. Obviously, the impedance diagram of Mg was composed of one high-frequency capacitive loop and an inductive arc at low frequency. As a comparison, the Sc-containing Mg alloys also included a capacitive loop in the medium-frequency region, which represented that the protective film was built up on the surface\(^1\). Correspondingly, the Bode plots are presented in Figure 5D. The |Z| versus frequency plot of the mMg-Sc alloy exhibited a relatively high value. For phase angle versus frequency, two wave crests (represent capacitive loop) and one wave trough (represent inductance loop) were included in Sc-containing Mg alloys. The Mg contains only one wave crest and one wave trough, which was consistent with the Nyquist plots.

In general, high-frequency capacitive loop was attributed to the electric double layer at the interface of Mg substrate and electrolyte\(^1\). The capacitive loop observed at the middle-frequency region was related to the presence of protective film\(^1\). The low-frequency inductance loop was ascribed to the chemical reaction of Mg\(^+\) with H\(_2\)O in the region of corrosion product film rupture and the desorption of corrosion products\(^1\). Moreover, the EIS spectra of the samples could be interpreted using the equivalent circuit, as shown in Figure 6A. In the equivalent circuit, R\(_s\) stood for solution resistance. The R\(_c\) and R\(_f\) represented the charge transfer resistance and the film resistance. The CPE\(_f\) was the associated constant phase element of product film, and CPE\(_d\) represents the double layer capacitance\(^2\). The L and R\(_s\) were the inductive elements, which represented inductance and inductance resistance.

The parameters were fitted by ZSimpWin software, and the results are summarized in Table 3. However, previous researchers reported that the CPE parameter did not completely describe the precise value of the capacitance, since the CPE behavior involves dielectric system dispersion or conductive system dispersion, which had a much narrower range of expected values for the dielectric constant\(^3\). Therefore, the capacitance could be replaced by C\(_f\) in the following equation\(^4\):

\[
C_f = \mathcal{Q}^{1/n} \left( \frac{R_f R_{f_0}}{R_s + R_f} \right)^{(1-n)/n}
\]  

(3)

Where, C\(_f\) was the effective capacitance of corrosion film in \(\mu\)F/cm\(^2\) and n was the CPE index. The calculation results of C\(_f\) for the samples are shown in Figure 6B. It was shown that Mg-Sc had the smallest C\(_f\) which was only 31.69 \(\mu\)F/cm\(^2\). Wang et al\(^5\) reported that the variation of C\(_f\) and film thickness was in inverse proportional relationship. The smaller C\(_f\) value indicated the thicker corrosion film formed on

| Table 2. Fitted Tafel parameters from the polarization curves depicted in Figure 2B. |
|-----------------|-----------------|-----------------|-----------------|------------------|
| Samples        | E\(_\text{corr}\) (V) | i\(_\text{corr}\) (A/cm\(^2\)) | E\(_\text{bd}\) (V) | P\(_i\) (mm/y) |
|----------------|--------------------|-------------------|-----------------|------------------|
| Mg             | -1.62              | 4.16×10\(^{-5}\)  | /               | 0.961            |
| Mg-Sc          | -1.58              | 7.94×10\(^{-5}\)  | -1.44           | 1.834            |
| mMg-Sc         | -1.52              | 1.31×10\(^{-5}\)  | -1.20           | 0.303            |
|----------------|--------------------|-------------------|-----------------|------------------|
the samples surface at the initial stage. To compare the samples impedance more intuitively, the polarization resistance ($R_p$) can be obtained by the following formulas:

$$R_p = R_f + \frac{R_{ct}R_f}{R_{ct} + R_f}$$

(4)

It was clear that mMg-Sc alloy had the largest value of $R_{ct}$, $R_f$, and $R_p$, as shown in Figure 6C, implying this alloy showed a better corrosion resistance. This was in good consistence with the results of polarization curves.

### 3.4 Degradation behavior

The *in vitro* degradation behavior was evaluated by immersion tests. The pH variation with soaking time was measured, as displayed in Figure 7A. Clearly, the pH of all the samples raised quickly at the initial stage, indicating that the dissolution of the Mg matrix was accompanied by the release of OH$^-$. With prolonged immersion time, the rate of increase in pH value decreased significantly. This was due to the formation of corrosion products, which inhibited further dissolution of the substrate. Then, the pH of all samples reached a stable value. It was noteworthy that the mMg-Sc alloy possessed a relatively low pH, which was consisted with the ion concentration results after immersion in the SBF solution for 168 h, as shown in Figure 7C. However, it did not imply that the corrosion has ceased. This indicated that an equilibrium was established between the formation of corrosion products and the dissolution rate$^{[56]}$.

The variation of hydrogen evolution volume versus immersion time was recorded, with the results shown in Figure 7B. The evolution of the hydrogen volume was approximately linear with the immersion time, which
indicated that the hydrogen generation volume was almost equal at the same time. In addition, the higher straight slope of the Mg-Sc alloy demonstrated that a great deal of unmelted Sc particles formed violent galvanic corrosion with the substrate. The corrosion rate evaluated from the hydrogen evolution and the weight loss is displayed in Figure 7D. It was noticeable that the average corrosion rate of $P_H$ was always lower than the $P_W$. This was mainly contributed to the inadequate gas tightness of the hydrogen collection device[^37]. Furthermore, the mMg-Sc sample owned a relatively low $P_H$ and $P_W$ corrosion rate of 0.61 mm/year and 0.72 mm/year, respectively. Thus, it could be inferred that the addition of rare earth Sc and MA treatment significantly enhanced the corrosion resistance of Mg alloy.

SEM was carried out to clearly observe the corrosion morphology. The surface morphologies after immersion in SBF for 168 h are displayed in Figure 8A. Obviously, the significant corrosion pits were formed at the boundary of the Sc particles due to the micro-galvanic corrosion. The high-magnification SEM images revealed that the corrosion products of Mg were sparse plate-like. As a comparison, the corrosion film of Sc-containing Mg alloys was more compact, which indicated that Sc was an important factor for corrosion film. Especially, the corrosion film of mMg-Sc was densest. The EDS analysis of regions A, B, and C showed that the Mg, O, Ca, and P elements were distributed in all samples, whereas the Sc-containing Mg alloys were rich in Sc (Figure 8B). Besides, the XRD was conducted to further analyze the products, as the results shown in Figure 8C. It was proved that the corrosion products of Sc-containing Mg alloys include $Sc_2O_3$, while only the $Mg(OH)_2$ was detected in Mg.

To understand the corrosion process, the cross-section SEM of Mg and Sc-containing Mg alloys is displayed in Figure 9A. It was clearly that the corrosion products of Mg and Mg-Sc alloy were relatively thicker and loose. As for the mMg-Sc alloy, the corrosion products were thinner, indicating that the damage to the matrix was softer due to the formation of a more uniform and dense corrosion layer. Based on the results of the above immersion tests results, a schematic model of the degradation process of mMg-Sc alloy was proposed, as shown in Figure 9B. Initially, the substrate was attacked by chloride ions in the SBF.
solution, which was accompanied by the generation of Mg$^{2+}$ and Sc$^{3+}$ ions. Then, the Mg$^{2+}$ ions combined with OH$^{-}$ ions to form Mg(OH)$_2$, while Sc$^{3+}$ reacted with oxygen ions to form Sc$_2$O$_3$. Due to chemical instability, Mg(OH)$_2$ was readily converted to MgCl$_2$ by chloride ions. The generation and decomposition of Mg(OH)$_2$ was a dynamic equilibrium process. Thus, the originally generated Mg(OH)$_2$ would be gradually replaced by Sc$_2$O$_3$, resulting in a more stable and compact corrosion layer.

3.5. Biocompatibility

The degradation of Mg alloys in vivo would release metal ions into the surrounding tissues, creating the risk of implant-related infections$^{58-60}$. Therefore, it was essential to assess the cytotoxicity of the rare earth element Sc, which was added in Mg alloys. The in vitro cytotoxicity of the high Sc-containing Mg alloys was evaluated by measuring the viability of BMSC cells after 1, 4, and 7 days exposure to a cell culturing medium, expressed as a percentage of cell viability in the control group. Based on ISO standard 10993-5, the biodegradable alloys were identified as non-cytotoxic, as the cell viability was higher than 70% of the control group$^{61-63}$.

As shown in Figure 10A, the fluorescent images of live/dead cell viability assays were used for qualitative assessment of the biocompatibility. Obviously, with incubation time extending, the green-stained live cells were increased progressively, whereas red-stained patches for dead cells were rarely detected. Besides, more spindle-shaped cells were observed in mMg-Sc group after 7 days’ culture as compared with the other two groups. The CCK-8 assay was carried out to quantitatively study the biocompatibility of Sc-containing Mg alloys, as displayed in Figure 10B. The cell viability of all samples increased with the decreasing of extracts concentration. As compared with Mg and Mg-Sc alloy, the mMg-Sc alloy had the maximum cell viability at the same extract concentration and time. This might be attributed to the better corrosion resistance of the mMg-Sc alloy, which was consistent with the results reported in the previous studies. The better corrosion resistance of Mg alloys would directly impact the cell viability, as they released a relatively low concentration of metal ions into the cell culture medium. Therefore, it was clearly proved that the Sc-containing Mg alloy would not impact the cell viability, as they released a relatively low concentration of metal ions into the cell culture medium. Therefore, it was clearly proved that the Sc-containing Mg alloy exhibits no adverse effects on cell viability in vitro and had an adequate biocompatibility. Prior studies have reported that the total Mg ion concentration in human body should be below 480 μg/mL, and the Sc ion concentration below 300 μg/mL was acceptable$^{64,65}$. In this work, the concentrations of Mg and Sc ions detected in the mMg-Sc alloy were 18 and 12 μg/mL, respectively, which were far below the maximum acceptable values in human body.
4. Conclusions

The Mg(Sc) solid solution powder was prepared through MA and subsequently consolidated by SLM. The degradation behavior and biocompatibility of the SLM processed Sc-containing Mg alloys were systematically studied. The conclusions are listed as below:

1. The XRD and TEM results of milled powders indicated that the single Mg(Sc) solid solution powder was prepared after ball milling for 40 h. The solid solution structure was maintained after SLM, which was due to its fast heating and cooling rate.

2. The immersion test results revealed that high Sc content addition significantly enhanced the corrosion resistance of Mg matrix because of the formation of protective corrosion product film, which contained rare earth oxide.

3. Sc-containing Mg alloys exhibited no adverse effects on cell viability in vitro and had an adequate biocompatibility, which was suitable for future orthopedic applications.

Acknowledgments

This study was supported by the following funds:

1. National Natural Science Foundation of China
(51935014, 52165043, 52105352, 82072084, 81871498); (2) JiangXi Provincial Natural Science Foundation of China (2020ACB214004, 20202BAB214011, 20212BAB214026); (3) The Provincial Key R & D Projects of Jiangxi (20201BBE51012); (4) The Project of State Key Laboratory of High Performance Complex Manufacturing; (5) Key Laboratory of Construction Hydraulic Robots of Anhui Higher Education Institutes.

**Funding**

This study was supported by the following funds: (1) The Natural Science Foundation of China (51935014, 52165043, 52105352, 82072084, 81871498); (2) Jiangxi Provincial Natural Science Foundation of China (2020ACB214004, 20202BAB214011); (3) The Provincial Key R & D Projects of Jiangxi (20201BBE51012); and (4) The Project of State Key Laboratory of High Performance Complex Manufacturing.

**Conflict of interest**

The authors declare that they have no competing financial interests that could have influenced the work reported in this paper.

**Author contributions**

C.J.S guided and reviewed the initial versions of the article; Y.Y and C.L designed and performed the experiments with assistance from M.Y; Y.Y C.L and L.Y completed the manuscript’s writing content; S.P and D.W supervised the project and contributed in language improvements. All authors have given approval to the final version of the manuscript.

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