

Review

# A Review of SLMed Magnesium Alloys: Processing, Properties, Alloying Elements and Postprocessing

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Abstract: Selective laser melting (SLM) is an additive manufacturing method with rapid solidification properties, which is conducive to the preparation of alloys with fine microstructures and uniform chemical compositions. Magnesium alloys are lightweight materials that are widely used in the aerospace, biomedical and other fields due to their low density, high specific strength, and good biocompatibility. However, the poor laser formability of magnesium alloy restricts its application. This paper discusses the current research status both related to the theoretical understanding and technology applications. There are problems such as limited processable materials, immature process conditions and metallurgical defects on SLM processing magnesium alloys. Some efforts have been made to solve the above problems, such as adding alloy elements and applying postprocessing. However, the breakthroughs in these two areas are rarely reviewed. Due to the paucity of publications on postprocessing and alloy design of SLMed magnesium alloy powders, we review the current state of research and progress. Moreover, traditional preparation techniques of magnesium alloys are evaluated and related to the SLM process with a view to gaining useful insights, especially with respect to the postprocessing and alloy design of magnesium alloys. The paper also reviews the influence of process parameters on formability, densification and mechanical behavior of magnesium. In addition, the progress of microstructure and metallurgical defects encountered in the SLM processed parts is described. Finally, this article summarizes the research results, and with respect to materials and metallurgy, the new challenges and prospects in the SLM processing of magnesium alloy powders are proposed with respect to alloy design, base material purification, inclusion control and theoretical calculation, and the role of intermetallic compounds.

Keywords: selective laser melting; magnesium alloys; properties

# 1. Introduction

Magnesium is one of the most abundant elements on Earth and represents approximately 2.5% of its composition. Magnesium and its alloys are lightweight metallic structural materials with certain advantages, such as low density, high specific strength and high stiffness [1,2]. Magnesium and its alloys are considered to have great application prospects in the aerospace, transportation, electronics, biomedicine, and energy fields due to their excellent physical and chemical properties, such as low density, good damping performance, biocompatibility, recyclability, large hydrogen storage capacity, and high theoretical specific capacity [3–5]. As the lightest structural material currently available, magnesium alloys have the potential to replace steel and aluminum in many structural applications [6]. Thus, magnesium alloys have already found considerable applications in various fields, including the aerospace, aircraft, automotive, and electronics fields; in particular, magnesium die castings have been widely used in the automotive industry [7]. However, despite the abovementioned advantages,



magnesium and its alloys still face many difficulties in large-scale industrial applications. For instance, the poor room temperature plasticity and poor corrosion resistance of these materials still need to be addressed [8,9]. Currently, magnesium alloy development is focused on the production of complex structures with high efficiency and minimal environmental impact; accordingly, many new magnesium alloy preparation technologies have emerged.

Additive manufacturing (AM) is a promising new technology that can dramatically change the way components are manufactured in many different industries and greatly increase manufacturing efficiency. According to different technologies, AM can be divided into electron beam melting (EBM), direct laser forming (DLF) and selective laser melting (SLM). SLM is a technology widely used in the preparation of metal powders. Commonly used metal powders include Fe-based alloys, titanium-based alloys, Al-based alloys, Mg-based alloys, and nickel-based alloys. SLM uses a high-energy laser beam to completely melt metal powder in a protective atmosphere along a defined laser path, and this molten metal rapidly solidifies [10]. By repeating this step and overlapping subsequent layers, a three-dimensional component is eventually formed. SLM provides a means of manufacturing geometrically complex structures, eliminating the need to build molds, which would otherwise require a considerable amount of time and money to manufacture. The cooling rate of the molten pool reaches  $10^3 - 10^8$  K/s due to the rapid movement of the laser and the molten metal pool [11]. The characteristics of rapid solidification and layered manufacturing enable the SLM process to produce materials with a more uniform chemical composition, a more concentrated solid solution, a refined microstructure, and better mechanical properties [12,13]. However, due to the inherent heat treatment of the SLM process, wherein each layer is cyclically reheated by the deposition of subsequent layers, the microstructure of the material is also unique [14]. To date, the samples produced by SLM still have some defects, such as pores and cracks, which affect the final use of the produced parts. Therefore, how to control the material density, microstructure and performance by adjusting the SLM process conditions is a research focus.

Due to several characteristics of magnesium alloys, including a low melting point, easy oxidation, and dangerous production, research on the preparation of these materials is still in its infancy worldwide. Research institutions investigating these materials include the Fraunhofer Institute for Laser Technology, Huazhong University of Science and Technology, University of Science and Technology Beijing, Central South University, Université de Technologie de Belfort-Montbéliard, Chongqing University, Hong Kong Polytechnic University, Suzhou University, and Delft University of Technology. Current research is in the small-scale trial production stage in the laboratory, and research and experimental data on the forming characteristics and mechanical properties of selective laser melted (SLMed) magnesium alloys are scarce. On the one hand, owing to the inherent physical properties of magnesium alloys, the research progress of SLMed magnesium alloys is limited. On the other hand, during the production of SLMed magnesium alloys, the generation of defects and the characteristics of microstructures affect the performance of SLMed magnesium alloys. For instance, in the Mg-Al-Zn(AZ) series of magnesium alloys, the presence of the second phase Mg<sub>17</sub>Al<sub>12</sub> limits the mechanical properties—especially the elongation—of the alloy, which restricts the further development of SLMed magnesium alloys. At present, many scholars have conducted research and comprehensive reviews on the spheroidization, defects, porosity, and alloying element loss in magnesium alloys and other metals prepared by SLM [15–21]. However, limited processable materials, immature process conditions and metallurgical defects are still problems that magnesium alloys need to face and solve in the SLM process. In the past two years, these three issues of SLMed magnesium alloys have been substantially improved by optimizing process parameters, introducing post treatment and adjusting different alloying elements. However, few review articles have been written in this regard. Therefore, it is necessary to summarize the development of SLMed magnesium alloys from the perspectives of process, element adjustment and post treatment. To improve the machinability of the material, this paper will review the research progress of the addition of alloying elements and the post-treatment to expand the processable magnesium alloy materials. Process conditions and new research progress on

relative density, microstructure, mechanical properties and corrosion resistance of SLMed magnesium alloys will be reviewed. In addition, the formation mechanism of metallurgical defects, especially oxidation and cracks, will be discussed and analyzed to provide a reference for the application of SLMed magnesium alloys.

This article also discusses the aspects that need to be addressed in future research on SLMed magnesium alloys, which provides a basis for further research and development of these materials.

#### 2. Formation and Energy Density of SLMed Magnesium Alloys

There are many process parameters that affect the forming of SLMed magnesium alloys. The selection of process parameters directly affects the balling degree, relative density, microstructure, and mechanical properties of magnesium alloys. The selection of the best process parameters is the key to ensuring good sample formation [22–24]. The most commonly studied process parameters are laser power, scanning speed, hatch spacing, and layer thickness. These four process parameters can be expressed by a comprehensive evaluation index: energy density  $E_v$ . The definition of  $E_v$  is shown in Equation (1):

$$E_v = \frac{P}{vHT}(J/mm^3) \tag{1}$$

where P is the laser power, v is the scanning speed, H is the hatch spacing, and T is the layer thickness. Energy density integrates the key process parameters, which can more intuitively reflect the energy applied by the laser to the powder, to evaluate the heating, melting, and evaporation of the powder. Tables 1 and 2 summarize the research progress of SLMed magnesium alloys in terms of alloy grades, powder characteristics, forming quality, performance, optimal energy density, and research institutions.

As shown in Tables 1 and 2, the research materials involve magnesium and its alloy powders, and different research institutions have studied the mechanical properties and corrosion resistance of SLMed magnesium alloys under best processing parameters. There are differences in the optimal energy input for forming magnesium alloys of the same alloy grade. First, the optimal energy input is related to the properties of the powder. Samples containing different particle sizes and particle size distributions require different amounts of energy to fully melt the powder. Second, there are differences in the research equipment used by different research institutions, which creates differences in process conditions. The introduction of different alloying elements into magnesium powder improves its mechanical properties and corrosion resistance. To further analyze the relationship between forming and magnesium alloy grade in Table 1 is determined, as shown in Figure 1.

We summarized the effects of energy input on the forming, relative density, microhardness, grain size, and mechanical properties of different magnesium alloy series. It can be seen that during the SLM process, the energy input will have certain macroscopic and microscopic effects on the magnesium alloy, including the formation of pores and microstructures. This will be analyzed and discussed in detail in the following chapters.

Types	Powder Shape	Partical Size (μm)	Processing	Relative Density (%)	Ultimate Tensile Strength (UTS) (MPa)	Yield Strength (YS) (MPa)	Elongation (EL) (%)	Microhardness (Hv)	Laser Power (W)	Scanning Speed (mm/s)	Energy Density (J·mm <sup>-3</sup> )	Refs.
AZ91	irregular	25-63	SLM	>99	$329 \pm 6$	$264 \pm 1$	$3.7 \pm 0.8$	_	100	800	104	[25]
WE43	irregular	25-63	SLM	>99	$307 \pm 6$	$302 \pm 3$	$11.9 \pm 1$	_	200	700	238	[25]
AZ91D	spherical	59	SLM	99.52	$296 \pm 2$	$254 \pm 4$	$1.8 \pm 0.2$	100	200	333	167	[26]
60	spherical	30	SLM	94.05	-	-	-	$78 \pm 10$	200	300	416	[27]
AZ61	spherical	48	SLM	$99.4 \pm 0.3$	$287 \pm 3$	$233 \pm 2$	$3.1 \pm 0.1$	_	150	400	156	[28]
AZ61	spherical	70	SLM	99 ± 5	-	-	-	$93 \pm 4$	80	3	9609.6	[29]
ZK60	spherical	50	SLM	$97.4 \pm 2$	-	-	-	$89.2 \pm 5$	50	8	600	[30]
ZK30-xAl	spherical	ZK30: 45–74; Al: 5–15	SLM	-	-	-	-	$75.7\pm6$	80	3	4004	[31]
Mg-9Al	Mg: irregular Al: spherical	Mg: 42 Al: 17	SLM	82 ± 3	-	-	-	$80 \pm 7$	120	300	93.75	[32]
Mg	spherical	25.8, 43.32	SLM	96.13	-	-	-	52.4	90	10	300	[33]
Mg	irregular	75-150	SLM	-	-	-	-	-			_	[34]
Mg	spherical	5-45	SLM	-	-	-	-	-	20	20	0.99J/mm <sup>2</sup>	[34]
Mg	spherical	5-45	SLM	-	-	-	-	0.87 ± 0.13 GPa	13–26	10-200	$1.27 \times 10^9 \text{ J/mm}^2$ (CW)	[35]
Mg	spherical	5-45	SLM	-	-	-	-	$0.95\pm0.08~\mathrm{GPa}$	13–26	10-200	$1.13 \times 10^{12} \text{ J/mm}^2$ (PW)	[35]
Mg	spherical	10-45	SLM	-	-	-	-	$0.72 \pm 0.07 \text{ GPa}$	18	1	118.2 J/mm <sup>2</sup>	[36]
Mg	spherical	1-10	SLM	_	-	-	-	48.3	50	5	100 J/mm <sup>2</sup>	[37]
Mg-2Ca	spherical	100-200	LAM	-	111.19	-	-	68	100	10	1200	[38]
Mg-xSn	spherical	Mg: ~10 Sn: ~1	SLM	-	-	-	-	65.7	60	11	107.4 J/mm <sup>2</sup>	[39]
Mg-3Zn-xDy	Mg-3Zn spherical Dy: irregular	Mg-3Zn: ~150 Dy: ~130	SLM	-	-	-	-	121.3 ± 3	20	3	360.4 J/mm <sup>2</sup>	[40]
AZ61	spherical	48	SLM + HIP	>99	$230 \pm 2$	$120 \pm 1$	-	$98.9 \pm 5.9$	-	-	156	[41]
ZK61-xZn	spherical	50	LAM	$69.1 \pm 1$	-	-	-	$106.8 \pm 2$	90	10	1146	[42]
Mg-Zn	spherical	Mg: ~50 Zn: ~31	SLM	$99.35 \pm 0.2$	$148 \pm 5$	-	$11 \pm 0.6$	$50 \pm 1$	180	700	183.7	[43]
Mg-Gd-Zn-Zr	spherical	44	SLM	99.95 (53.3 J/mm <sup>3</sup> )	$332 \pm 5$	$325 \pm 5$	$4 \pm 0.2$	-	80	300	88.9	[44]

Table 1. Summary of research progress on SLM magnesium and magnesium alloy powder.

Note: CW represents continuous wave, PW represents pulsed wave, and HIP represents hot isostatic pressing.

Types	Powder Shape	Particle Size (µm)	Processing	<b>Biodegradation Rate</b>	Refs.
AZ61	spherical	70	SLM	$12.26 \text{ mg/cm}^{-2}$	[29]
ZK60	spherical	50	SLM	$0.006 \text{ mL cm}^{-2} \text{ h}^{-1}$	[30]
ZK30-xAl	spherical	ZK30: 45–74; Al: 5–15	SLM	$0.17 \pm 0.02 \text{ mg cm}^{-2} \text{ day}^{-1}$	[31]
Mg	irregular	75-150	SLM	Fail	[34]
WE43	spherical	25-60	SLM	0.17 mL/cm <sup>2</sup>	[45]
ZK60-Cu	spherical	ZK30: 50; Cu: 80 nm	SLM	Close to 1.01 mm $y^{-1}$	[46]

Table 2. Summary of the biodegradability of SLMed magnesium alloys.



**Figure 1.** Energy density range of the SLMed magnesium and its alloys [26,28,32,37]. (This picture was drawn by the author; the data in the figure come from citations).

Figure 1 summarizes the energy density required for the formation of several common magnesium alloys during SLM. The forming characteristics of the SLMed magnesium alloy show five feature areas with increasing energy density. These five feature areas can be divided into a strong balling zone, a balling zone, a transition zone, a forming zone and an evaporation zone. Balling refers to some spherical particles existing on the surface of the SLMed sample. There are many mechanisms affecting spheroidization. Severe spheroidization is closely related to the powder characteristics, laser energy density, scanning strategy, wettability between powders, and the Marangoni effect, and there have been many conclusions about spheroidization [16,47–49]. The following summarizes how to control the occurrence of spheroidization from the process point of view and the relationship between the types of spheroidization, pores and other defects and process parameters.

A series of balling particles agglomerate to form a large molten pool of solid–liquid phase or near-liquid phase. The lack of wettability between the molten pool and the previous layer causes a balling effect [19]. The formation of magnesium alloy in the SLM process of each region is summarized hereafter, and the forming characteristics of the SLMed magnesium alloy are shown in Figure 2.

Strong balling zone: SLM forming in the range of high scanning speeds or low laser powers (low energy density), which is characterized by insufficient heating of the magnesium alloy powder, and the temperature of some powders does not reach the melting point temperature and fails to completely melt [26]. Taking AZ61 as an example, when the scanning speed is as high as 1000–1800 mm/s, in fact, the forming is in a solid–liquid state and there is poor bonding between the powder particles, so the sample has a powder accumulation structure without any mechanical strength at this processing parameters; moreover, some samples have a loose metal structure [32]. Balling is a complex metallurgical process that is caused by the instability of the molten pool and the Marangoni effect. The surface characteristics are shown in Table 3 and Figure 2a,e. Liu et al. [28], under an optical microscope,

revealed that the pore (size greater than 100 µm) shape of the sample surface in the strong balling area was mostly meniscus-shaped [50]. A similar phenomenon was also found in the preparation of SLMed ZK60 magnesium alloy [27]. At a high speed of 900 mm/s (low energy density), the surface of the magnesium alloy was covered with irregularly shaped pores due to incomplete powder melting, the relative density decreased significantly to 82.25%, and the evaporation was very weak in this region. In addition, too high a scanning speed will cause pores on rough surfaces [30]. A significant heat-affected zone (HAZ) also formed during the orbital melting process. The HAZ was formed by partial melting of particles due to thermal conduction from the center of the molten pool to the adjacent powder. Low energy density also means that the scanning speed was too fast or the laser power was too low. If the scanning speed is too fast, due to the low density and chemical activity of magnesium, more powder is blown upwards and oxidized to form black fog (MgO), contaminating the mold cavity [33]. Balling also occurs at very low scanning speeds because the liquid surface energy and liquid lifetime are reduced in a short length range [51]. Balling occurs due to thermal stress and weak interlayer bonding, resulting in surface deterioration. Therefore, the scanning speed cannot be too high to ensure sufficient energy input.



**Figure 2.** Forming characteristics of SLM magnesium alloy. When the scanning speed is 1400 mm/s, 900 mm/s, 550 mm/s and 250 mm/s respectively, the hatch spacing is 0.06 mm (**a**–**d**); hatch spacing of 0.08 mm, (**e**–**h**); and hatch spacing of 0.1 mm, (**i**–**l**). Reproduction from [28], with permission from Elsevier (Amsterdam, The Netherlands), 2020.

Balling zone: Compared with the strong balling zone, this zone has decreased scanning speeds (800–950 mm/s) or increased laser power (increased energy density to 50–78.13 J/mm<sup>3</sup>). Due to the decrease in scanning speed, the interaction time between powder and laser is prolonged, and the temperature of some particles is higher than the melting point, which causes the powder to partially melt. In this case, adjacent particles are sintered together due to the formation of a small amount of liquid [37]; however, the balling zone is still in a liquid–solid state. For SLMed AZ91, the energy density in this range was 66–77 J/mm<sup>3</sup>, and the molten pool with a smaller circumference was unstable under relatively low energy input [26]. At the same time, the balling particles tended to grow along the direction of the scanning trajectory, which was attributed to the melting track breaking up into discrete droplets [52]. Therefore, the balling particles parallel to the scanning direction together with the large amount of unmelted powder induced more severe surface deformation (Figure 2f). The number of defects decreased when the scanning speed and hatch spacing decreased (i.e., the energy density  $E_v$  increased), because the wettability between the powder and the substrate improved and the balling

effect weakened. The decreased scanning speeds (increased energy density) caused the powder to be sufficiently heated and melted, and the adjacent scanning tracks overlapped, thereby reducing the internal pore size. In addition to the reduction in the internal pore size, the surface pore size was also reduced with the decreased scanning speeds [30]. It is note that the size of the pores was also related to the vertical height of the sample, and the size of the pores increased with increasing printing height [18]. The cause of this phenomenon is still related to energy. Based on the characteristics of the layered manufacturing technology, the thin layer produced by the initial printing layer directly contacts the substrate and melts rapidly. As the number of printing layers increases, the heat transferred from the substrate to the powder decreases, and the powder to incompletely melt, thereby forming pores. In addition, the adjustment of energy input is achieved by adjusting process parameters. Therefore, the key to controlling the forming quality is to adjust the optimal scanning speed and laser power to provide suitable forming energy density for magnesium alloy.

Transition zone: In this zone, for the AZ61, the scanning speed further decreased (550–750 mm/s). A "hill" formed between the scanning trajectories, which was composed of a series of "melt beads" instead of a completely continuous melting track [34]. Under the effect of decreased scanning speeds, energy input increased, so the instantaneous temperature gradient from the center of the track to the edge increased, the surface tension decreased, the viscosity of the metal droplets decreased, and the surface "melt beads" (ball-shaped particles) were linked together under a smoother flow, which resulted in the formation of scanning trajectories at the "hill" and "valley" positions (Figure 2d,k). Hence, the morphology of the location of the "hill" part was affected by the processing parameters. However, for the Mg-9Al alloy, due to the high scanning speed, even if the laser power is reduced below 30 W (the energy density is small), the forming quality cannot be optimal.

Forming zone: In this region, the powder completely melted into a liquid phase under sufficient and suitable processing parameters (scanning speed of 250–500 mm/s) (Figure 2i). For AZ series magnesium alloys, as the scanning speed decreases, the forming quality becomes better. For Mg-9Al alloy, the laser power is reduced to a lower level (10–20 W), and the best sample can be obtained by adjusting the scanning speed. The temperature of the liquid phase was a certain level above the liquidus temperature. Then, the liquid phase rapidly diffused and solidified, and the melted powders were well combined to form a continuous and smooth trajectory [37]. As the scanning speed decreases or the laser power increases, the interaction time between the powder and the laser increases, and the heat received per unit time increases. Therefore, the energy density in this region increased the temperature of the powder bed and reduced the viscosity of the melt pool, so the molten part can be spread in the layer, thereby promoting more effective densification of the solid powder particles. However, distortion of scanning trajectories caused by flocculated deposition and metal powder evaporation can still be found on some sample surfaces [26].

Evaporation zone: As the laser power continued to increase or the scanning speed continued to decrease, the energy input became excessive and increased the temperature of the molten pool, causing the molten alloy system to reach the temperature of the vapor line, resulting in the evaporation of some alloy components. For Mg-9Al alloy, when the laser power is higher than 60 W, even if the scanning speed increases (~1000 mm/s), the evaporation phenomenon cannot be avoided. Magnesium has a low boiling point (1093 °C) and a high vapor pressure, and the magnesium component was severely evaporated during the forming process when the energy density was too high. This evaporation led to rapid expansion of the system, which caused a recoil pressure on the molten pool [26]. The molten pool was blown away from the surrounding unmelted powder, and the SLMed magnesium alloy failed. In the protective gas chamber, MgO powder and fog were formed. At this time, the Mg:Zn ratio in the sample increased due to evaporation [27]. After each layer of powder was sintered, only an extremely thin metal layer solidified on the substrate, and the shape was irregular [32]. The excessive energy input also reduced the viscosity of the molten pool because of the combined effect of excessive

shrinkage of the melting track and high residual stress. The melting track will completely melt or even break, resulting in many visible cracks [24] and deformation.

There is a close relationship between the processing parameters (scanning speed and laser power) and the forming quality of SLMed magnesium alloy samples. The forming characteristics of magnesium alloys vary with respect to different processing parameters. In addition, the optimal energy density for suitable forming of magnesium alloy was 83–250 J/mm<sup>3</sup>. From the above summary, it can be seen that the effects of laser power and scanning speed should be considered comprehensively in order to obtain the best quality samples. For magnesium alloys, only changing the laser power or scanning speed may not be able to obtain the best forming quality, and it is necessary to comprehensively adjust these two process parameters. However, research on the influence of laser power on SLMed magnesium alloy forming is still lacking, and needs to be further studied. It can also be seen that there were some differences in the processing parameters of different grades of magnesium alloys during the SLM process. The main consideration was how to adjust the scanning speed and laser power to get the suitable energy density, find the most suitable melting, wetting, spreading, bonding, and solidification conditions, and finally form a magnesium alloy sample with high relative density and good surface quality. These issues are discussed in the following sections.

Surface Feature	Alloy	Scanning Speed (mm/s)	Energy Density (J/mm <sup>3</sup> )	Unmelted Powder	Pores	Balling	
	AZ61	1000-1800	35–45	Lots of	Lots of, ~14%, >100 µm, connected to each other, a network	Spherical: ~100 μm Ellipsoidal: 100–300 μm	
Strong Balling zone	AZ91	1000	38–58	Lots of	Lots of, ~10%	Spherical: ~100 μm Ellipsoidal: ~300 μm	
	Mg-9Al	-	-	-	-	-	
	AZ61	800–950	63–78	Less	Less, ~4%, <50 µm,	Spherical: <50 µm	
Balling zone	AZ91	833	66–77	Lots of	Lots of, ~4%	Spherical: ~100 µm	
·	Mg-9Al	15–20 W: 160–1000	3–47	-	Poor bond neck	Powder stacking	
	AZ61	550-750	83–114	None	None	Less/scanning tracks	
Transition zone	AZ91	-	-	-	-	-	
Transition Zone	Mg-9Al	10 W: 40 15–30 W: 80	63–94	-	Loose metal structure	-	
	AZ61	250-500	125-250	None	None	None	
Forming zone	AZ91	333–667	83–167	None	None	None/flocculent depositions, scanning tracks	
	Mg-9Al	10 W: 10 15 W: 20–40 20 W: 40	94–250	None	None	-	
	AZ61	-	-	-	-	-	
Evaporation zone	AZ91	~166	214-429	Fail	Fail	Fail	
	Mg-9Al	90-110 W: 0.01-1	~2750	Fail	Fail	Fail	

Table 3. Processing parameters and forming quality of SLMed magnesium alloy [26,28,32].

## 3. Properties of SLMed Magnesium Alloy

#### 3.1. Relative Density of SLMed Magnesium Alloy

Relative density is often used as an indicator of the quality of SLMed parts. The relative density is the ratio of the density obtained by SLM to the theoretical density of the bulk material. The theoretical density of a material can be calculated from the atomic weight and crystal structure of the material. Figure 3 summarizes the trend of the relative density of different series of magnesium alloys as a function of energy density. The relative density ranged from 73 to 99%, and the variation in relative density under different energy densities was large.

Figure 3 shows that the energy density under the SLM process has an important effect on the relative density of the magnesium alloy [26–28,30,32,44]. From the perspective of the AZ61, AZ91, ZK series, Mg-9Al alloys and Mg-Gd-Zn-Zr with increasing energy density, the relative density of the alloy increased.



Figure 3. Relationship between energy density and relative density [26-28,30,32,44].

Additionally, Figure 3 shows that in the curve of the relative density of magnesium alloy samples as a function of energy density, the initial slope of the curve was very high. As the energy density increased, it generally increased rapidly at first and then tended to flatten or even slightly decrease. The temperature of the molten pool will change accordingly when the energy density changed [53,54]. The impact of energy density on the relative density of SLMed magnesium alloys can be considered from two aspects: (1) the macroscale effects of the energy density on the melting of the powder; and (2) the microscale effects of the energy density on the solid solution of the elements, which affects the relative density of the SLMed magnesium alloys.

The increase in scanning speed and hatch spacing reduced the peak temperature and temperature gradient of the melt. When the scanning speed and scanning distance were large (lower energy density) [55], heat and mass transfer occurred due to surface tension. Generally, higher surface tension near the edge of the molten pool will pull the molten liquid out of the center of the molten pool, and cracks occur because adjacent melting tracks cannot overlap. Moreover, as the hatch spacing increased, the cracks became wider, which directly affects the final relative density of the sample [56]. The high dynamic viscosity of the laser melt pool was considered to be the main reason for the cracks formed at high scanning speeds (low energy density). The definition of dynamic viscosity is shown in Equation (2) [30]:

$$\mu = \frac{16}{15} \sqrt{\frac{m}{kT}} \lambda \tag{2}$$

where  $\mu$  is the dynamic viscosity,  $\lambda$  is the surface tension, k is the Boltzmann constant, m is the atomic mass, and T is the temperature of the liquid pool. At low energy density  $E_v$  (higher scanning speed), the temperature T in the molten pool was relatively low, and the magnesium alloy molten liquid had a high dynamic viscosity, which was not conducive to the smooth diffusion of the liquid. Additionally, incomplete melting resulted in the formation of large balling particles, and the scanning trajectory was discontinuous. Therefore, it was easy to form pores, and the relative density was low.

As the laser energy density increased, the powder melted more fully, the liquid phase fluidity improved and penetrates into the voids between the particles, so the pores were dispersed and the pore size was reduced, forming a relatively smooth surface, and the density of the magnesium alloy also increased [16].

However, when the hatch spacing was too small, a large amount of molten liquid migrated to the original scanning trajectory at a higher speed, resulting in the accumulation of molten liquid, which affected the density of the magnesium. At high energy densities, the molten pool widened, forming a

temperature gradient in the molten pool, exacerbating the change in surface tension, which caused balling and solidification at the edge of the molten pool [57].

The relative density is also related to the solid solution of the elements. A study reported that the relative density increased as the solid solution of Al increased [28]. For the AZ series magnesium alloy, the change in relative density with respect to energy density was no longer obvious after the relative density of the material reached approximately 98%. The relative density of the material decreased when the energy density increased from 100 to 178 J/mm<sup>3</sup>. The decrease in relative density was also related to the solid solution of Al. According to the solid solution theory, Al can be dissolved into the  $\alpha$ -Mg matrix as a substitutional atom. During rapid solidification, the solid solution of Al will increase in the  $\alpha$ -Mg matrix due to the solute retention effect [58,59]. At a suitable energy density, the increase in the melt temperature and the solute retention effect work together to increase the solid solution of Al in the magnesium alloy matrix. However, if the energy density is further increased, the solid solution of Al will decrease due to the weakened solute retention effect. The density of Al is 2.7 g/cm<sup>3</sup>, which is higher than the density of pure Mg (1.7 g/cm<sup>3</sup>) [60,61], so the solid solution of Al will increase the relative density of the sample.

It can be seen that the energy density has an effect on the relative density of the SLMed magnesium alloy. If the energy density is too low, the powder cannot be fully melted, the system is in a solid–liquid two-phase state, and the surface tension and viscosity of the liquid increase, resulting in the liquid not flowing smoothly and agglomerating into spheres. At the same time, pores are formed, which ultimately results in the sample not being dense. However, the energy density is too high, the powder will evaporate. Moreover, the solute capture effect is weakened, and the relative density of the sample is reduced due to the decrease in solid solution elements. Therefore, the preparation of dense magnesium alloys requires the energy density to be controlled in a suitable range, the solid solution of Al to be enhanced, and the surface tension to be reduced so that the liquid diffuses at a stable rate and fills the pores, thereby eliminating pores and spherical particles between the tracks [57].

According to the current research results, for AZ61 and AZ91, the relative density of the alloy was close to the theoretical density when the energy density was approximately 100–200 J/mm<sup>3</sup>. However, the relative density of the ZK series and Mg-9Al alloy was only approximately 75–93% at this energy density. Consequently, the optimal energy density must be determined for the different alloy components in the SLM process.

# 3.2. Microhardness of SLMed Magnesium Alloy

From the perspective of the SLM preparation process, the energy density also has an important effect on the microhardness of different magnesium alloys, as shown in Figure 4 [26,30,32,33,37,41].



**Figure 4.** (a) Effect of energy density on microhardness; (b) enlarged image of the gray area in (a) [26,30,32,33,41].

The enlarged view in Figure 4b shows that the microhardness decreases slightly with increasing energy input. This phenomenon was mainly attributed to the growth of grain size and the weakening of the solute capture effect. Figure 5 shows the effect of energy density on grain size. [25,26,28–30,32,37–40,44].



Figure 5. Effect of energy density on grain size [25,26,28-30,32,37-40,44].

First, Figure 5 and Table 4 show that the grain size of magnesium alloys of different alloy series was affected by temperature and increased with increasing energy density. The grain size of SLMed magnesium alloy was mainly 1–15  $\mu$ m, and the maximum grain size was 30  $\mu$ m [26]. Compared with as-cast samples, the SLMed samples had significantly smaller grains. According to the Hall–Petch formula, grain refinement can significantly improve microhardness. Conversely, coarsening of the grain size causes a decrease in microhardness. With the introduction of alloying elements, the grain size of the SLMed magnesium alloy changed [31,40]. The grain size of magnesium alloys increased as the Dy content increased, and the microhardness decreased significantly (Figure 6a) [40]. Microhardness is also affected by microstructure. In the same magnesium sample, the microhardness changed with respect to the microstructure at different positions [26,29,62]. This phenomenon is due to different locations in the same sample experiencing different thermal histories. During the SLM process, the microhardness at the center of the molten pool and the microhardness at the edge zone fluctuated, which was caused by the refinement of the microstructure at the center of the molten pool compared with the microstructure of the edge zone [26].

Alloy	Energy Density (J/mm <sup>3</sup> )	Grain Size (µm)
AZ91 [26]	104–167	1–1.2
WE43 [25]	238	1
ZK60 [30]	420-750	2–8
ZK30-xAl [31]	4004 Al(wt.%): 0-7	$21.6 \pm 2.6 - 7.3 \pm 1.0$
ZK61-xZn [42]	1146 Zn(wt.%): 5–30	1.1-6.1
Mg-9Al [32]	94-250	10–20
Mg [37]	60-120	5–20
Mg-2Ca [38]	1200	5
Mg-xSn [39]	107 Sn(wt.%): 0–7	5–25
Mg-3Zn-xDy [40]	360 Dy(wt.%): 0–5	6.4–18.1
AZ61 [41]	138–208	1.6–2.5
Mg-Gd-Zn-Zr [44]	27–267	$1.3 \pm 0.4$ -2.3 $\pm 1.0$

Table 4. Processing parameters and grain size of various SLMed magnesium alloy powders.

Second, because of the "solute capture" effect caused by rapid solidification, the solid solution of the elements in the matrix was enhanced, so the microhardness increased. Al and Zn, as common alloying elements, were solid-solved into the magnesium alloy matrix. The atomic radii of Al and Zn are 0.1199 and 0.1187 nm, respectively, which are smaller than that of Mg (0.1333 nm) [63]. Therefore, lattice distortion will occur when these elements are dissolved into the Mg matrix. The Al concentration in the SLMed magnesium alloy was much higher than that in the as-cast sample because of the rapid solidification during SLM. According to the solid solution strengthening theory, higher solid solubility results in better mechanical strength [26,64]. With increasing energy density, the solid solubility of the alloying elements increased, and the microhardness of the sample was enhanced by solid solution strengthening. For Mg-Al alloys, the change in microhardness is directly proportional to the Al content in  $\alpha$ -Mg [65]. In Mg-Zn-Zr alloys [30], the increase in the solid solubility of Zn in  $\alpha$ -Mg is also conducive to increasing hardness. Based on the solid solution strengthening theory, the lattice distortion caused by the solid solution of Zn limits the dislocation slip in the crystal grains, thereby increasing the hardness of the SLMed ZK60 [64]. However, if the energy density is further increased, the temperature of the molten pool will be further increased, the solute trapping effect will be weakened, the solid solution of alloying elements such as Al and Zn will be reduced [28], and the microhardness will be slightly reduced (Figure 4a).

Third, the distribution of the second phase plays a crucial role in the microhardness of SLMed magnesium alloys. Due to the different distribution of intermetallic phases, the microhardness value of magnesium alloys prepared by SLM fluctuated within a certain range, and the amplitude increased as the intermetallic phase volume fraction increased, as shown in Figure 6b. As the Dy content increased, the volume fraction of the Mg-Zn-Dy phase continued to increase, and the dispersed second phase mainly precipitated at the grain boundaries, inhibiting the movement of the grains, which enhanced the microhardness of the alloy [40]. The intermetallic compound in Mg-Al alloys is usually  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub>, and its microhardness is different from that of the  $\alpha$ -Mg matrix. It can be seen from the nanoindentation experiments and hardness mapping in Figure 7 that the average hardness of the second phase  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> precipitated in the AZ91D magnesium alloy was 174 ± 103 Hv, which was significantly higher than the average hardness of the matrix  $(123 \pm 13 \text{ Hv})$  [62]. The hardness of the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase was reduced to 150 ± 60 Hv by applying selective laser surface melting (SLSM) treatment to the magnesium alloy, whereas the hardness of the  $\alpha$ -Mg phase was maintained at 126  $\pm$  3 Hv. Although the SLM process reduced the dispersion of the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase, it did not change the average hardness of the matrix. This indicates a reduction in element segregation and residual stress. On the other hand, the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase was modified by SLSM, which reduced the hardness and dispersion of the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase, and the phase distribution of the magnesium alloy was more uniform and continuous [62]. By introducing 0–7 wt.% Al in ZK30 magnesium alloy, the average microhardness gradually increased from 59.7 to 75.7 Hv [31]. An intermetallic hard-brittle  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase was formed after the addition of Al, which was distributed in the soft  $\alpha$ -Mg matrix and acted as a strengthening phase in the alloy [66], resulting in increased strength and microhardness. In the ZK series magnesium alloy, the second phase was  $Mg_7Zn_3$  [30]. The  $Mg_7Zn_3$  phase, which has high hardness and a uniform distribution, can strengthen the structure by hindering the dislocation motion between grains.

In addition, the presence of defects also affects microhardness. The porosity generated in the sample at low energy density and the cracks formed due to residual stress in the sample at high energy density will result in reduced hardness [37].

In summary, the microhardness of the magnesium alloy was affected by rapid solidification during the SLM process, which mainly affected the microstructure and the solid solution of the elements. On the one hand, the significant refinement of the microstructure of magnesium alloys was due to the rapid solidification, which made the microhardness of the SLMed magnesium alloy significantly higher than that of the traditional as-cast magnesium alloy. On the other hand, the solute trapping effect in the SLM process resulted in the solid solution of the alloying elements in the matrix, and the different solid solutions of the alloying elements have different strengthening effects. Furthermore, the distribution and amount of the second phase and the presence of defects will also affect the microhardness. The hardness of the second phase was generally higher than that of the matrix, and the microhardness of the magnesium alloy was generally improved by suppressing the dislocation motion between the grains. As the second phase content decreased, the microhardness distribution of the material became more uniform.



**Figure 6.** Relationship between grain size, second phase and microhardness of the magnesium alloy: (a) grain size and (b) second phase volume fraction. Reproduction from [40], with permission from Taylor & Francis (London, UK), 2020.



**Figure 7.** Hardness distribution of the matrix and second phase in AZ91 magnesium alloy. (**a**) Scanning electron microscopy (SEM) image of the as-cast samples and (**b**) corresponding nanoindentation hardness mapping. (**c**) SEM image of the SLSM samples and (**d**) corresponding hardness mapping. Reproduction from [62], with permission from Elsevier, 2020.

# 3.3. Mechanical Properties of SLMed Magnesium Alloy

Due to their lightweight characteristics, magnesium alloys can reduce fuel costs, and the total life cycle cost of Mg parts is lower than that of parts made of other materials [67]. Therefore, magnesium alloys are widely used in the automotive and aerospace fields. Weight reduction not only saves energy but also reduces greenhouse gas emissions. Reducing the weight of a car by a certain amount will result in a similar improvement in fuel economy [68]. Magnesium alloy parts can usually be used in engines, seat frames, gearboxes, etc. Good strength, ductility and castability are prerequisites for the use of magnesium alloys. However, there are few studies on the mechanical properties of SLMed

magnesium alloys, and the amount of experimental data available for reference is limited. According to the existing research, the strength of SLMed magnesium alloys is significantly higher than that of as-cast magnesium [26,28,69] without losing plasticity [25,26,28].

As shown in Figure 8 and Table 5, when the scanning speed was 333–800 mm/s, and energy density was 104–167 J/mm<sup>3</sup>, the ultimate tensile strength (UTS) and yield strength (YS) of the SLMed AZ91 magnesium alloy reached 296–330 MPa and 254–264 MPa, respectively. The UTS and YS of SLMed AZ91 were approximately 30% and 50% higher than those of as-cast AZ91 magnesium alloys [25,26], but the elongation of the SLMed samples (1.24–1.83%) was approximately 40% lower than that of as-cast samples (3%), as shown in Figure 9. The AZ61 magnesium alloy prepared by SLM also exhibited the same trend. When the energy density was 156 J/mm<sup>3</sup>, the UTS and YS reached 287 MPa and 233 MPa, respectively, which was 93% and 135% higher than those values in the as-cast AZ61 magnesium alloy [69]. However, the elongation was 3.28–2.14%, which was lower than the elongation of the as-cast AZ61 (5.2%). The increase in strength was the result of grain refinement and solid solution strengthening. First, on account of the nature of the SLM process, melting and solidification at a smaller size resulted in fast solidification, which made the microstructure of the entire part more uniform. For the magnesium alloy forming process, segregation of alloying elements occurred on a much smaller scale. The chemical composition of the whole part was more uniform, and the amount of solid solution elements increased, so the strength of the SLMed parts was higher than that of the as-cast parts [70]. Second, Figure 3 shows that the grain size of the SLMed magnesium alloy was significantly refined. The as-cast grain size was usually 200–300 µm [71,72], whereas the grain size after SLM treatment was mostly 1–15  $\mu$ m, and the average grain size of the AZ series magnesium alloy was approximately 2 µm. According to the Hall–Petch formula, the grains were refined, and the strength of the material was improved. The difference in the strength between different SLMed samples was mainly due to the different SLM process conditions, which led to deviations in density and microstructure, such as defects, structure and grain size [73]. Wei et al. [26] found that at different energy densities, the strength of magnesium alloys increased slightly with increasing energy density. The UTS and YS of the SLMed AZ91 magnesium alloy increased from 274 MPa and 237 MPa (83 J/mm<sup>3</sup>) to 296 MPa and 254 MPa (167 J/mm<sup>3</sup>), respectively. In fact, compared to the energy density, the laser power and scanning speed (linear energy density) are the main factors that change the characteristics of the melt pool, leading to significant changes in the microstructure and mechanical behavior of the manufactured samples. Therefore, it is necessary to combine these two process parameters for comprehensive analysis. When the scanning speed increases or the laser power decreases (low energy density), the interaction time between the laser and the powder is shortened, the heat accumulation in the molten pool is less and the temperature gradient is smaller, and the crystal grains do not have enough time to grow, which is conducive to grain refinement. As the cooling rate is faster, the higher the cooling rate during solidification, the shorter the time available for grain coarsening. In terms of solid solution elements, the cooling rate of the molten pool is faster at higher scanning speeds, and the solid solution elements in the matrix solidify before they can completely diffuse, resulting in an increase in the solid solution elements in the matrix, achieving the purpose of solid solution strengthening. However, it is still necessary to pay attention to the problem of pores caused by too high scanning speed or too low laser power, which results in the powder being unable to be fully heated and melted. The influence of laser power and scanning speed on microstructure will be discussed in detail in subsequent chapters. An analysis of the fracture behavior of SLMed parts showed that SLMed AZ91 exhibited mixed ductile-brittle fracture. The ultimate compressive strength (UCS) and elastic modulus of SLMed Mg-Ca alloys also increased with increasing laser power (energy density) [38]. This phenomenon was mainly due to the different porosities under different energy inputs. With the increase in laser power, the porosity decreased, resulting in an increase in the UCS, elastic modulus, and plasticity of the porous Mg-Ca alloy.

<b>Table 5.</b> Summary of the processing parameters and	properties achieved for various SLMed magnesium
alloy powders [26,28,32].	

Alloy	Laser Power (W)	Scanning Speed (mm/s)	Energy Density (J/mm <sup>3</sup> )	UTS (MPa)	YS (MPa)	EL (%)
AZ91 [26]	200	333-667	83-167	$274 \pm 7 - 296 \pm 3$	$227 \pm 3 - 254 \pm 4$	$1.2 \pm 0.1  1.8 \pm 0.2$
AZ91 [25]	100	800	104	329	160	$1.8 \pm 0.2$
AZ61 [28]	150	300-450	138-208	$239 \pm 3-296 \pm 2$	$217 \pm 3 - 233 \pm 2$	$3.1 \pm 0.1$
Mg-2Ca [38]	50-100	10	625–1125	5-46 (UCS horizontal) 51-111 (UCS longitudinal)	-	-



Figure 8. Effect of energy density on strength [26,28,38].



Figure 9. Effect of energy density on elongation [25,26,28].

It was also found that the mechanical properties of magnesium alloys were different in different directions, indicating that the alloy had significant anisotropy [38]. However, the elastic modulus under longitudinal compression and the UCS did not change much when the energy density increased from 875 to 1125 J/mm<sup>3</sup>. The longitudinal stress–strain curve at 1125 J/mm<sup>3</sup> had a larger yield platform than the other curves. This variation should mainly be ascribed to the different porosities at different energy

inputs and the different distribution modes of the pores under transverse compression and longitudinal compression. The distribution of pores also made the longitudinally compressed skeleton part denser than the laterally compressed skeleton part. Therefore, the longitudinal mechanical properties were better than the transverse mechanical properties. The existence of pores caused stress concentrations, which greatly reduced the mechanical properties of the magnesium alloy; the mechanical properties increased with decreasing porosity. Consequently, the pore size of the porous Mg-Ca alloy can be adjusted by adjusting the laser parameters or energy density, thereby reducing the porosity and ultimately improving the mechanical properties of the porous material.

The fracture morphology of the SLMed magnesium alloy showed that there were obvious cleavage planes around the reserved pores of the porous Mg-Ca alloy, indicating cleavage fracture [38]. River morphology and dimples can be observed on the fracture surface inside the pores of the porous Mg-Ca alloy. The number of longitudinally compressed dimples was significantly greater than the number of transversely compressed dimples. These dimples indicate a certain degree of plastic deformation before fracture, and the plasticity under longitudinal compression was better than that under transverse compression. As the laser power increased, the number and size of dimples increased. This finding indicates that as the energy input increased, the plasticity of the porous Mg-Ca alloy increased. This is because under the increased laser power, the powder receives more sufficient energy per unit time to melt the powder and combine with each other, so the reduction of macroscopic defects leads to an increase in plasticity. In conclusion, the SLMed porous magnesium alloys exhibited a mixed brittle–ductile fracture.

Nevertheless, the elongation of SLMed magnesium alloy is usually low (Figure 9), which may be related to the presence of micropores in the part and the presence and distribution of the second phase. Fractures mostly occur in areas with high porosity. Moreover, for the AZ series magnesium alloy, the research in [28] showed that the existence and distribution of the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase had a substantial influence on the plasticity. The  $\alpha$ -Mg matrix is relatively soft, and its crystal structure is a close-packed hexagonal structure. The brittle and hard  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase has a cubic crystal structure. The  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase in magnesium alloys prepared by SLM usually precipitates along the grain boundaries and is connected to form a network. The crystal structures of the  $\alpha$ -Mg and  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub>); moreover, due to the formation of high dislocation density and stress concentrations at the interface of  $\alpha$ -Mg and  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> [74], cracks nucleated and propagated along the phase interface [75–77]. As shown in Figure 10, the second phase precipitated along the grain boundaries, and the cracks were generated at the interface between the two phases.



**Figure 10.** Optical microscopy fractographs showing that the microcracks were prone to initiate near the Mg/Mg<sub>17</sub>Al<sub>12</sub> interface and the grain boundaries: (**a**) the rear part; (**b**) the middle part; (**c**) the impact part. Reproduction from [75], with permission from Elsevier, 2020.

A side-view of the fracture morphology also confirmed the limitation of the  $\beta$  phase on plasticity. The existence of pores and cracks in the fracture and the second phase at the bottom of the dimple verified the effect of defects and the  $\beta$  phase on plasticity. Furthermore, some fine grains and large

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grain boundaries formed by small equiaxed grains were observed, for which the fracture occurred along the crystal. This fracture morphology has also been reported in magnesium alloys prepared by other methods [78,79]. After the grains were refined, the stress was dispersed.

During the deformation process,  $\alpha$ -Mg grains first undergo plastic deformation, but the deformation is hindered when they encounter the second phase at the grain boundaries, resulting in incomplete deformation and fracture. A similar situation exists in laser-welded Mg alloys, wherein the fracture strain reduced from 13.6 to 3.3% due to the higher number of intermetallic precipitates causing embrittlement of the fusion zone [17]. Therefore, to obtain good plasticity in the Mg-Al alloy, the precipitation of Mg<sub>17</sub>Al<sub>12</sub> should be restricted. It is possible to improve the solidification rate by improving the process parameters or by applying post-treatment methods such as solution heat treatment to increase the solid solution of Al, thereby reducing the formation of Mg<sub>17</sub>Al<sub>12</sub> at the grain boundaries. Studies have shown that the elongation of Mg alloys is closely related to the content of Mg<sub>17</sub>Al<sub>12</sub>. When the proportion of Mg<sub>17</sub>Al<sub>12</sub> increases to approximately 9%, the ductility decreases [80]. However, under the condition of ensuring the quality of sample forming, higher scanning speed and lower laser power can produce a faster cooling rate, thereby inhibiting the occurrence of phase transition and reducing the precipitation of the second phase along the grain boundary. This part of the content will be in-depth analysis combined with the phase diagram in Section 5.

At present, there is no related research on the effect of heat treatment on the mechanical properties of SLMed magnesium alloys. This is an issue worthy of further exploration in the future. Hot isostatic pressing (HIP) can reduce the number of pores and decrease the anisotropy of the material [81], which has an impact on mechanical properties. In addition, plasticity can be improved by introducing different alloying elements. The literature [82] showed that solute Nd had a significant softening effect on the nucleation critical resolve shear stress (CRSS) of the cone <c + a > slip. When designing a high ductility magnesium alloy, from the perspective of reducing the strength difference between the soft deformation mode and hard deformation mode, the important factors that must be account for include the alloying elements, the solute concentration, and the predeformation strain.

## 3.4. Corrosion

As a lightweight material, magnesium is widely used for structural materials in various applications, including the automotive and aerospace fields, due to its low density, good heat dissipation, damping and electromagnetic shielding properties. In the biomedical field, osteoconductive implant materials are popular, and the biocompatibility and corrosion resistance of these materials are the research focus in this area. Recently, magnesium-based alloys have attracted interest as possible replacements for some of the metallic alloys in use due to the former being lighter and exhibiting a higher modulus of elasticity [83]. The corrosion behavior of magnesium can be divided into galvanic corrosion, stress corrosion, biocorrosion, etc.

In moist environments, magnesium and its alloys always form a thin surface film. This natural outer layer is not dense because its corresponding Pilling–Bedworth ratio is ~0.81, which indicates that the underlying metal cannot be completely covered. As a result, magnesium and its alloys are highly susceptible to corrosion. Due to the dissolution of magnesium, a loose film consisting mainly of Mg(OH)<sub>2</sub> is formed on the surface of magnesium alloy. The poor corrosion resistance of magnesium alloy is mainly caused by the following two reasons. First, the quasipassive hydroxide film formed on the magnesium surface is much less stable than the passive film on the surface of metals such as aluminum and stainless steel. Second, internal galvanic corrosion is caused by intermetallic phases or impurities. Therefore, the improvement of corrosion resistance can also be solved through two aspects. First, the passivation of the surface film is affected by the alloying elements in the magnesium alloy. For example, Hara et al. [84] claimed that adding Al to Mg or increasing the Al content in the Mg matrix can change the composition and structure of the surface film, thereby improving the resistance of the film to local breakdown. Cai et al. [85] asserted that Zn could effectively improve the surface

protection film and corrosion resistance of Mg alloys. The effect of alloying elements on corrosion resistance will be discussed in detail in Section 4.

Second, the corrosion resistance can be improved by reducing impurity elements. Elements such as Fe, Ni, and Cu are usually present as intermetallic precipitates, which are harmful because of their low hydrogen overvoltage [86]. The effect of intermetallic compounds on corrosion behavior is complex. The second phase can serve as both a barrier to prevent corrosion of magnesium alloy and as a cathode to accelerate corrosion of magnesium alloy. Hence, the corrosion resistance of Mg alloys is usually related to the type, size and morphology of the intermetallic phase [87,88]. The  $\beta$  phase is expected to be a barrier when there is a small grain size and relatively large  $\beta$  phase fraction, and more importantly, when the  $\beta$  phase is in the form of a continuous network along the Mg grain boundaries. However, microgalvanic corrosion is readily accelerated as the  $\beta$  phase agglomerates and is separately distributed in the Mg matrix with large grain sizes. It is noted that the decreased cathodic and anodic reactions of Mg-Al-Mn-Ca alloy produced by the spinning water atomization process (SWAP) were attributed to the fine dispersion of Al<sub>2</sub>Ca particles and the supersaturated Al content in the  $\alpha$ -Mg matrix, respectively, resulting in superior corrosion resistance [84]. Therefore, the second phase of the dispersed distribution is beneficial to improve the corrosion resistance of the magnesium alloy.

In terms of biological corrosion, the key point is that an implant must possess the appropriate strength for an adequate period of time to allow healing to take place. During this time, the corrosion rate must be sufficiently slow to not affect the healing process. While it is true that the byproducts of magnesium corrosion are nontoxic, as the metal corrodes, the pH in the localized area increases, and this basic environment may impede healing. Similarly, hydrogen gas evolves during the corrosion process and must be eliminated. When Mg alloy was soaked in an aqueous physiological environment, the following reactions occurred, as shown in Equations (3)–(5):

$$Mg(s) + 2H_2O(l) \rightarrow Mg(OH)_2(s) + H_2(g)$$
 (3)

$$Mg(s) + 2Cl^{-}(aq) \rightarrow MgCl_{2} + 2e^{-}$$
(4)

$$Mg(OH)_2 (s) + 2Cl^- (aq) \rightarrow MgCl_2 + 2OH^-$$
(5)

It was reported that the anodic dissolution of magnesium in aqueous solutions occurs concurrently with cathodic hydrogen evolution and is accompanied by an anomalous phenomenon called the negative difference effect (NDE), which is characterized by an unexpected increase in the cathodic hydrogen evolution reaction as the anodic overvoltage increases [89].

Rapid solidification has been identified as an effective method for improving the strength and corrosion resistance of magnesium alloys used in structural applications or corrosive environments [90]. The rapid solidification during SLM can refine the microstructure and dissolve the second phase. Moreover, by rapid solidification, the mechanism of corrosion can be changed essentially from pitting corrosion of Mg-A1 alloys into overall corrosion [91]. Izumi et al. [92] indicated that the change in cooling rate had a great influence on the corrosion behavior of magnesium alloys. Increasing the cooling rate can delay the occurrence of filamentous corrosion due to grain refinement and the formation of a supersaturated single  $\alpha$ -Mg phase solid solution in mg alloys. In addition, laser-induced rapid solidification can also increase the solid solubility of alloying elements, such as manganese and aluminum, and promote the formation of more protective and self-healing thin films, thereby limiting the occurrence of local galvanic corrosion. The corrosion resistance of magnesium alloys prepared by SLM is summarized in Table 2. Shuai et al. [30] studied the corrosion resistance of SLMed ZK60 magnesium alloy at different energy densities. The results indicated that the hydrogen volume evolution rates were in the range of 0.006–0.0019 mL·cm<sup>-2</sup>·h<sup>-1</sup> as the laser energy input varied from 420 J/mm<sup>3</sup> to 750 J/mm<sup>3</sup>. The optimal energy density for corrosion resistance was 600 J/mm<sup>3</sup>. The lowest hydrogen evolution volume rate was 0.006 mL·cm<sup>-2</sup>·h<sup>-1</sup>. The refined grains, homogenized microstructure and extended solid solution obtained by rapid solidification contributed to the enhanced corrosion resistance of the SLMed ZK60 alloy. He et al. [29] investigated the corrosion resistance of

SLMed AZ61 magnesium alloy when the laser power was 50–90 W. It was reported that the minimum degradation rate occurred at 80 W, whose values corresponding to 24 and 144 h were approximately 2.4 and 1.2 mm year<sup>-1</sup>, respectively. This phenomenon occurred due to the elimination of pores and the refinement of the microstructure. When the laser power was 90 W, the microstructure became coarse, and the corrosion resistance decreased.

SLM is a process that can effectively improve the corrosion resistance of magnesium alloys, and the corrosion of magnesium alloys is a complicated process. Therefore, the advantages of the SLM process should be fully used to develop new magnesium alloys or improved alloys to produce finer grains and new phases. Furthermore, research should focus on developing more feasible, reliable, maintainable, and lower-cost protection systems.

## 3.5. Factors that Affect Performance Defects

## 3.5.1. Cracking

The existence of cracks in SLMed alloys will affect the subsequent application of the material. Wang et al. [93] researched the reasons for premature material failure. The premature failure schematic diagram is shown in Figure 11. This is due to external defects (pores and unmelted particles) that act as sites for crack initiation. Then, cracks propagated through grain boundaries and/or cellular boundaries that contain continuous brittle second phases. Therefore, cracks are a problem worthy of attention. Mg-Zn binary alloy is a kind of Mg alloy that easily cracks during solidification [94]. This could be explained by the large solidification temperature range, high thermal expansion coefficient, and large solidification shrinkage of these alloys. For the SLM process, if there is sufficient stress at high laser energy density, the melt will crack.



**Figure 11.** Schematic diagram of SLMed Ag-Cu-Ge alloy premature failure: (**a**) low-magnification SEM image of fracture surface; (**b**,**c**) dimples and cleavage features; (**d**,**e**) samples after polishing; (**f**,**g**) external defects (pores and unmelted particles); (**h**,**i**) internal defects of TEM micrographs; (**j**) Schematic illustration depicting crack initiation at external defects and crack propagation along internal defects. Reproduction from [93], with permission from Nature Publishing Group (London, UK), 2020.

Shuai et al. [30] found the presence of microcracks in the samples of SLMed ZK60 magnesium alloy. When high *Ev* was used, considerable thermal stress was generated and accumulated in the rapidly solidified SLMed layer. When the thermal stress exceeded a certain threshold, a hot crack

formed. Wei et al. [43] observed cracks in Mg-Zn binary alloys. The morphology of the SLMed Mg alloy with different Zn contents is shown in Figure 12.



Figure 12. Cracks in SLMed (a) Mg-1Zn, (b) Mg-2Zn, (c) Mg-4Zn, (d) Mg-6Zn, (e) Mg-8Zn, and (f) Mg-10Zn. Reproduction from [43], with permission from Elsevier, 2020.

When the Zn content was different, the cracks in the Mg-Zn binary system were also different. The schematic diagram is shown in Figure 13. At a 1 wt.% Zn content, because the Mg<sub>7</sub>Zn<sub>3</sub> eutectic phase was less abundant and mostly granular, the liquid eutectic phase during the final stage of the solidification process was discontinuous and low in content. Therefore, the strength of the mushy zone can resist the solidification shrinkage stress, thereby inhibiting the formation of cracks. As the Zn content increased, the area fraction of the  $Mg_7Zn_3$  eutectic phase increased, which means that in the final stage of SLM pool solidification, the strength of the mushy zone decreased, leading to the formation of solidification cracks. However, at the same time, the fluidity of the residual liquid was significantly enhanced in the final stage of solidification. As a consequence, when the content of Zn was sufficiently high (12 wt.%), the solidification cracks may be backfilled by the residual liquid during the final stage of solidification, thereby alleviating the cracking tendency. The melting point and thermal expansion coefficient of aluminum are similar to those of magnesium. A similar situation usually occurs in SLMed aluminum alloys. The application of 7075 aluminum alloy is limited by cracking [95,96]. Yuki et al. [95] noted that for 7075 alloy, the optimal silicon content was 5%, which is conducive to eliminating cracks and improving mechanical properties. If the Si content was insufficient, the cracks cannot be completely eliminated. In contrast, excessive Si content resulted in brittleness. Microcracks are commonly attributed to solidification cracking and liquation cracking. The cause of solidification cracking is a residual thin film of liquid phase between the primary crystallized grains, and liquation cracking is caused by cyclic heat input, which occurs in multilayer welding and layered fabrication. The reason for the decrease in strength due to the heat input is mainly due to the eutectic phase or partial remelting of the component with a lower melting point. These melting points serve as the starting points for cracking. Generally, the morphology of the top of the sample can be used

to distinguish the two kinds of cracks. The surface layer is not affected by thermal conduction from subsequent layers during fabrication; therefore, the solidification structure that is created by single laser irradiation has been preserved. If cracks appeared on the surface, the influence of the cyclic heat input was excluded, indicating that the cracks were solidification cracks. If microcracks appeared in the lower layer, it indicates that the sample were affected by the cyclic heat input, producing fused cracks. Kimura et al. [97] investigated the relationships between the Si content and the mechanical properties of Al-Si binary alloy samples fabricated by SLM. They noted that the additions of silicon enhanced the proof stress and UTS of SLMed samples because the silicon elements enriched the proportion of the secondary phases, providing compositional reinforcement for the aluminum matrix. The Si helped eliminate microcracks in the Al alloys. The addition of Si induced the formation of eutectics with a low melting point and high fluidity, which decreased the crack sensitivity as these eutectics melted and filled the cracks during the final stage of the solidification process [96]. In addition, the selection of process parameters was also very important. As the laser power increased, more low-melting-point eutectic phases melted, which was conducive to the elimination of cracks. In the SLM process, due to the lack of diffusion during nonequilibrium rapid solidification, the actual liquid and solid phase temperatures were further reduced [98]. Therefore, during SLM processing of magnesium alloys, the critical temperature range was larger, and the solidification cracking sensitivity was higher. The addition of alloying elements can narrow the critical solidification range and alter the melt pool composition to avoid cracking [96,98,99]. Therefore, future studies should consider introducing other alloying elements to SLMed Mg-Zn binary alloys to eliminate microcracks. Moreover, it is necessary to study the parameter windows of different magnesium alloys.



Final stage of the solidification of SLM pools

**Figure 13.** Schematic diagram illustrating the effect of Zn content on the solidification cracking behavior of the SLMed Mg-Zn alloys. Reproduction from [43], with permission from Elsevier, 2020.

#### 3.5.2. Oxide Inclusions

It is well known that magnesium is highly susceptible to oxidation; therefore, elaborate protection from the atmosphere is required [100]. This is achieved using inert gases. Good shielding can avoid burning or porosity. Studies by Ng, CC, and others have shown that there are a large number of oxides in SLMed magnesium, and they tend to form between scan traces rather than between layers. It is also believed that the oxides will form on top of the molten pool, which may slow oxide diffusion, change the wettability and form a porous structure with weak mechanical properties [35]. Liu et al. [28] detected the presence of oxygen in both the Mg matrix and the second phase. The oxygen content in the matrix was 0.58 wt.%, whereas that in the second phase was 0.71 wt.%. Louvis et al. [101] observed that the formation of oxide films on both solid and liquid metal surfaces resulted in oxide films between the laser hatches in every layer of the SLMed Al parts; hence, pores were formed where two oxide films met. For existing oxide films, since the formation of oxide films is completely unavoidable, the SLM process must break these films, which requires high laser power, in order to produce a completely dense part. Therefore, to solve the issues pertaining to the unavoidable oxide films, further research on SLMed Mg should mainly focus on a new method of controlling the oxidation process and destroying oxide films formed within the components.

The oxygen in the SLM process comes from two sources: the oxygen in the molding chamber and the oxygen in the magnesium alloy powder. For the oxygen content in the molding chamber, high-purity protective gas is needed to reduce the presence of oxygen, but it cannot be completely avoided. It is believed that the oxygen content in the powder will lead to pores and reduce the mechanical properties of the sample [102–104]. Dong et al. [102] studied two 12CrNi2 alloy steels prepared via laser melting deposition (LMD) AM: one with high O content (5300 ppm) and the other with lower O content (280 ppm). Studies show that porous alloy steel was additively manufactured using high-O content powder. Using low-O content powder prevents gas pore formation in printed steel. Steel mechanical properties increased when the powder O content decreased [102]. Cao et al. [103] confirmed that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> formed on the surfaces of Al powder particles. Oxidation of an as-gas atomized Al powder prevented the transformation of interparticle boundaries (IPBs) into γ-Al<sub>2</sub>O<sub>3</sub> nanoparticle-containing grain boundaries in the bulk Al prepared by spark plasma sintering and led to the formation of continuous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layers with nanopores at the IPBs, causing a dramatic decrease in the elongation to fracture. Rao et al. [104] asserted that the desired combination of mechanical properties obtained by the use of low oxygen content powder showed its potential for exploring the near net shape advantage of HIP technology for alloy 718 components. In terms of oxygen content control, producing a vacuum in the molding chamber and adopting a powder purification process [12] can be considered. Please note that the presence of oxygen generally leads to the formation of inclusions, which degrade the properties of the material. However, it has also been reported that the introduction of ordered oxygen complexes enhances the plasticity and strength of high-entropy alloys [105]. Therefore, the effect of oxygen on magnesium alloys prepared by SLM and the control of oxygen content in a suitable range still require further research.

## 3.5.3. Other Factors

There are many other factors affecting the properties of SLMed alloys, such as alloying element loss [26,27], porosity [38,41], and spheroidization [47–49]. These factors, which are discussed in the previous sections, are related to each other. For instance, the consumption of alloying elements will lead to the instability of the scanning track and the high porosity of laser-machined parts [106]. The occurrence of spheroidization is generally accompanied by the appearance of pores [28]. At present, there are no scientific measures to avoid the loss of magnesium alloy during SLM processing. The dominant mechanisms for pore formation during SLM processing of Mg alloys need to be thoroughly investigated. There is no clear relationship between the porosity type and the SLM process parameters. Much work remains to be done in these areas.

#### 4. Effect of Alloying Elements on the Properties of SLMed Magnesium Alloy

Rapid laser melting is an effective way to improve the corrosion resistance of magnesium alloys. The rapid heating and cooling characteristics of laser processing can shorten the processing time to seconds or milliseconds, which is conducive to the refinement of grain size. Grain refinement is the key to improving corrosion resistance [39]. In addition, rapid laser melting can reduce composition segregation, which creates conditions for improving the overall performance of magnesium alloys by adding alloying elements. At present, further adding different alloying elements on the basis of SLM preparation can further optimize the properties of magnesium alloys, thereby obtaining high-performance magnesium alloys. This research direction has been very popular in the past two years. The effects of the addition of alloying elements such as Al, Ca, and Sn on the properties of SLMed magnesium alloys are discussed hereinafter. The number and depth of studies on the effect of adding alloying elements on SLMed magnesium alloys is still limited.

### 4.1. Regular Elements

#### 4.1.1. Alloying Element: Al

Al is a solid solution strengthening element that will produce precipitation strengthening at low temperatures (<393 K) and has a small impact on corrosion resistance. Al has a large solid solubility in solid Mg, and its ultimate solid solubility is 12.7%. Moreover, with decreasing temperature, the solid solution of Al decreases significantly, and the solid solubility at room temperature is approximately 2.0%. Aluminum can improve the castability and increase the strength of magnesium alloys. The higher the aluminum content, the better the corrosion resistance. However, the stress corrosion sensitivity increases with increasing aluminum content.

The AZ series of Mg alloys is most often used for casted and wrought applications because of its good castability and good mechanical properties [107,108]. The Al concentrations in the AZ series promote the formation of the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase, and the amount of this phase present in the alloys affects the deformation texture. High Al concentrations favor the formation of the Mg<sub>17</sub>Al<sub>12</sub> intermediate phase, which weakens the basal texture by inhibiting twin boundary motion and hindering formability. Hence, AZ alloys with high Al concentrations are preferred for engineering applications [109].

Aluminum is often used in different magnesium alloys because it has a significant positive effect on the degradation and mechanical properties of magnesium alloys [110,111]. As an alloying element, aluminum can improve the mechanical properties of magnesium alloys through solid solution strengthening and microstructure refinement [112,113]. In addition, Al is an effective reinforcing element in Mg alloys because it has a significant effect on changing its grain size and intermetallic phase [114]. The effect of Al on the structure and properties of Mg alloy can be attributed to the influence of the Al itself and the intermetallic compound  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> introduced by its addition.

Shuai et al. [31] noted that the grain size and intermetallic phase were the two key factors affecting the biodegradation behavior of magnesium alloys after the introduction of aluminum. Al (0–7 wt.%) was introduced into an SLMed Mg-Zn alloy, and the effect of the Al content on the structure and properties of the SLMed ZK30-xAl magnesium alloy was obtained. The results showed that the grain size and intermetallic phase volume fraction varied with respect to the amount of Al. As the aluminum content increased, the grains were refined, and the intermetallic phase volume fraction increased. When the Al content was less than 3 wt.%, the intermetallic compound  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> precipitated and dispersed, and grain refinement was the main factor affecting the degradation behavior. The finer grains led to an increase in the grain boundary density, the alloy was easily passivated, and the degradation rate was reduced. The Pilling–Bedworth ratio of Mg is less than 1, which means that its oxide layer has high compressive stresses, resulting in the formation of cracks [115]. The grain-refined alloy had a higher grain boundary density, which is beneficial to reduce the compressive stress to compensate for the mismatch between the oxide/base metal. Therefore, the reduction in the mismatch can improve the performance of the oxide film, which offers greater protection from the detrimental action of chloride ions and improves the degradation rate. The grain size was refined as the Al content increased further, and  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> continuously precipitated along the grain boundaries and formed a network when the Al content increased to 7 wt.%. At this time, the intermetallic phase  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> became the main factor affecting the degradation behavior. The larger intermetallic phase volume fraction caused severe galvanic corrosion and accelerated the corrosion process. Therefore, the degradation rate increased when the Al content increased to 5–7 wt.%. ZK30-3Al had the lowest degradation rate ( $0.17 \pm 0.02$  mg cm<sup>-2</sup> day<sup>-1</sup> in Table 2) and the lowest corrosion current. Therefore, with the introduction of Al, the degree of grain refinement increased and the degradation behavior improved, but the degradation rate gradually deteriorated when the Al content became excessive. In terms of mechanical properties, the microhardness of SLMed magnesium alloy increased with increasing Al content. This phenomenon was mainly caused by grain refinement, solid solution strengthening, and brittle, hard  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase strengthening. The reasons for this increase was previously analyzed in detail.

Similarly, we can refer to the influence of alloying elements in the traditional manufacturing process. Homayun et al. [114] studied the effects of different additions of Al on the microstructure, mechanical properties, degradation behavior and biocompatibility of as-cast Mg-4Zn-0.2Ca alloy. Their results showed that to improve the degradation behavior and mechanical properties of the alloy, the Al content should be controlled below 3 wt.%. The addition of Al increased the tensile strength of the alloy from 157 to 198 MPa. The mechanical properties of the magnesium alloys were optimal when the Al content was 3 wt.%. The addition of aluminum had a positive effect on the refinement of the alloy microstructure. However, an excessive amount of aluminum led to a considerable amount of second phase  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> formed at the grain boundaries, which substantially deteriorated the performance of the alloy. When the Al content exceeded 3 wt.%, the intermetallic compounds at the grain boundaries of the alloy formed a network, resulting in deterioration of the mechanical properties and accelerated current corrosion. In fact, although the precipitation of secondary phases in the alloy increased its corrosion potential, the corrosion resistance of the alloy was significantly reduced. Zhao et al. [116] surmised that the intermetallic compound ( $\beta$ -Mg<sub>17</sub>Al<sub>12</sub>) in AZ91 could be used as a cathode to accelerate the degradation rate or as a barrier to prevent degradation depending on the volume fraction and morphology of the second phase. Lu et al. [117] also found that as the intermetallic volume fraction of ZK30 increased, the degradation resistance decreased.  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> has an important influence on the degradation behavior and corrosion resistance of Mg alloys. For Mg-Al alloys, the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase was discretely distributed along the grain boundaries, which led to severe galvanic corrosion [118].

In addition, the presence of the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase will affect the mechanical properties of Mg. The increase in Al content led to the formation of a considerable amount of  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase compounds. The cubic crystal structure of  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> is incompatible with the close-packed hexagonal structure of Mg alloys. The lack of coherence between the crystal structure of the second phase and that of the magnesium alloy resulted in the formation and propagation of cracks under tensile stress. The  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase at the grain boundaries interconnected to form a network, which led to a significant reduction in elongation and strain [77]. Liu et al. [28] asserted that the reason for the lower plastic elongation of the SLMed AZ61 magnesium alloy than that of the as-cast sample was due to the precipitation of the second phase along the grain boundaries. As a result, crack sources were generated at the interface of the  $\alpha$ -Mg and  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phases, the plasticity was reduced, and the precipitation of the second phase increased as the Al content increased [31]. The negative effect of  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> on the mechanical properties of alloys has also been reported in other studies [85,112,119]. Therefore, when introducing Al, attention should be paid to the influence of  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> on the properties of SLMed magnesium alloys.

In addition to helping to refine the grains, Al also has a certain effect on the shape of the grains [120]. With the increase in aluminum content in magnesium-based alloys, the grains transformed from columnar to equiaxed morphologies. Increasing the solute content of Al enhanced the component undercooling and promoted heterogeneous nucleation during solidification and grain refinement.

Therefore, the precipitation and distribution of the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase should also be considered when Al is introduced to refine the grains during SLM. The amount of Al added should be controlled within a reasonable range to reduce the precipitation of the second phase  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> to reduce galvanic corrosion and intergranular crack growth.

# 4.1.2. Alloying Element: Ca

Magnesium alloys have poor room temperature plasticity and poor corrosion resistance, which limits their application and development to a certain extent. Researchers have found that the introduction of Ca into Mg alloys can significantly improve the plasticity, corrosion resistance and overall performance of Mg alloys [121–123]. Ca, an alkaline earth metal, is an element that can notably improve the mechanical properties of Mg-Mn alloys [124]. Ca not only improves the ignition point and high-temperature oxidation resistance of Mg alloys but also plays an important role in the grain refinement of Mg alloys [38,123,125]. Ca has a low solubility in Mg of approximately 0.43 at.% (~0.71 wt.%) at 517 °C [126] (radius ratio is greater than 15%). Ca has a strong affinity for Mg, and Ca can be used as a structural modification element or a dispersed phase to improve the thermal resistance and the yield limit of the alloy [127]. Adding Ca to Mg alloy can form intermetallic compounds such as Mg<sub>2</sub>Ca to strengthen Mg-Al and Mg-Zn alloys [128–130]. A previous study [38] investigated the properties of SLMed Mg-Ca porous alloys. The grain size of the porous magnesium-calcium alloys was  $5-30 \mu$ m, which was significantly lower than the grain size of as-cast magnesium alloys (300–500  $\mu$ m); in contrast, the grain size of SLMed pure magnesium was 10–20 µm [32]. The microhardness of the SLMed pure magnesium was between 60 Hv and 68 Hv, which was higher than that of as-cast pure magnesium. Grain refinement and solid solution strengthening were the main strengthening mechanisms of Mg-Ca alloys. At an energy density of 1125 J/mm<sup>3</sup>, the transverse UCS and elastic modulus reached 45.75 MPa and 0.973 GPa, respectively, and the longitudinal UCS and elastic modulus reached 111.19 MPa and 1.264 GPa, respectively.

Ca is an essential element in the human body that has no adverse biological effects, so it can also be used as an alloying element in orthopedic implant materials. Yang et al. [122] reported that the addition of Ca improved the corrosion behavior of Mg-Al-Mn alloys because the Ca reacted with the original alloy to form a new second phase as a sacrificial anode. Since CaO and Ca act on Mg alloys in a similar manner, CaO introduced in Mg alloys will react with Mg and Al to form a fine (Mg, Al)<sub>2</sub>Ca phase [131,132]. However, the potential of the (Mg, Al)<sub>2</sub>Ca phase was lower than that of the Mg<sub>17</sub>Al<sub>12</sub> phase, which led to reduced potential difference and enhanced corrosion resistance [133].

Shuai et al. [118] introduced 0–12 wt.% CaO into SLMed Mg-Al-Zn (AZ61) alloy. Their results showed that when the content of CaO was less than 6 wt.%, the precipitation of the second phase at the grain boundaries changed from dispersion to a slender branch-like structure. The introduction of CaO changed the discrete Mg<sub>17</sub>Al<sub>12</sub> phase into a continuous (Mg, Al)<sub>2</sub>Ca phase and then to a coarsened Mg<sub>2</sub>Ca phase (9–12 wt.% CaO). The  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> content decreased with the addition of CaO. In the SLM process, CaO reacted with Mg and Al in Mg-Al alloys, as shown in Equations (6) and (7).

$$Mg + 2Al + CaO \rightarrow Al_2Ca + MgO$$
 (6)

$$3Mg + CaO = Mg_2Ca + MgO$$
(7)

The formation of the second phase  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> was suppressed, since reaction (6) consumed a certain amount of Al, and the formation of the (Mg, Al)<sub>2</sub>Ca phase was promoted. As shown in reaction (7), the addition of CaO will oxidize Mg, and the resulting Ca will form Mg<sub>2</sub>Ca with Mg. Due to the double consumption of Mg, the formation of the Mg<sub>17</sub>Al<sub>12</sub> phase was also suppressed to a certain extent.

The corrosion resistance mechanism of Mg alloy after adding different CaO contents is shown in Figure 14. Different phases and microstructures have different corrosion potentials, resulting in different corrosion rates. The introduction of CaO transformed the discrete Mg<sub>17</sub>Al<sub>12</sub> phase into a

continuous (Mg, Al)<sub>2</sub>Ca phase and then to the coarsened Mg<sub>2</sub>Ca phase. The distribution of the second phase in AZ61, AZ61-3CaO and AZ61-6CaO was discontinuous and discrete. At this time, the corrosion behavior was mainly dominated by galvanic corrosion. In the initial stage, a galvanic couple was formed between the second phase (cathode) and the  $\alpha$ -Mg matrix (anode) due to a potential difference.  $\alpha$ -Mg grains were preferentially dissolved due to their low potential. As the adjacent Mg particles dissolved, most of the second phase disintegrated. The potential of the (Mg, Al)<sub>2</sub>Ca phase was lower than that of the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase, which reduced the potential difference between the  $\alpha$ -Mg and the second phase, resulting in weakened galvanic corrosion. Hence, AZ61-3CaO and AZ61-6CaO exhibited better corrosion resistance than AZ61. In AZ61-9CaO Mg alloys, electrochemical corrosion occurs between (Mg, Al)<sub>2</sub>Ca and  $\alpha$ -Mg grains in the initial stage. Once the exposed  $\alpha$ -Mg grains were corroded, the  $(Mg, Al)_2Ca$  phase, which is inert to the corrosion solution and has a continuous network distribution, acted as a barrier layer to prevent further penetration of the corrosion solution. AZ61-9CaO exhibited better corrosion behavior. For AZ61-12CaO, the Ecorr of Mg<sub>2</sub>Ca was lower than that of Mg [134]. The Mg<sub>2</sub>Ca phase replaced the  $\alpha$ -Mg phase as the anode and formed a galvanic couple with the (Mg, Al)<sub>2</sub>Ca phase. Mg<sub>2</sub>Ca dissolved preferentially, leaving voids along the grain boundaries. When the volume fraction of the Mg<sub>2</sub>Ca phase was sufficiently high to wrap the  $\alpha$ -Mg grains, the enclosed  $\alpha$ -Mg grains would fall off once the surrounding Mg<sub>2</sub>Ca phase was dissolved, resulting in an accelerated corrosion rate. The lowest corrosion rate of 0.031 mg cm<sup>-2</sup> h<sup>-1</sup> was observed when the CaO content was 9 wt.% [118].



**Figure 14.** Schematic diagram of the corrosion process of AZ61-CaO. Reproduction from [118], with permission from Taylor & Francis, 2020.

The influence of Ca on the plasticity of SLMed alloys is still lacking. However, this influence can be interpreted from the corresponding mechanism in traditional manufacturing processes. In addition to improving the corrosion resistance of Mg alloys, Ca also has a notable effect on plasticity [135]. The poor formability of magnesium alloys at room temperature limits their wider application. The deformation of magnesium alloys at room temperature is mainly achieved by  $\{0001\} < 11\overline{2}0 >$  basal slip and  $\{10\overline{1}2\} < \overline{1}011 >$  tension twinning [136,137], whereas the activation of nonbasal slip modes is generally difficult. Studies have shown that the addition of Ca greatly improves the elongation of Mg alloys [138–140]. Pan et al. [138] prepared an extruded Mg-1.0Ca (wt.%) binary alloy with a tensile elongation of 18.0% and a grain size of 2 µm. Zhang et al. [139] found that the extruded Mg-1.0Zn alloy has an elongation of 16.2% and a grain size of 20–50 µm. The grain size of the extruded

Mg-1.0Zn-0.2Ca (wt.%) alloy was refined to 5–20  $\mu$ m after adding Ca, and the elongation increased to 35.5%. The elongation was 119% higher than that of the extruded Mg-1.0Zn alloy. The high ductility of the Mg-Zn-Ca ternary alloy can be attributed to the texture weakening and grain refinement caused by the segregation of Ca at the grain boundaries [140]. The high ductility of Mg-Al-Ca ternary alloys and Mg-Ca binary alloys indicates that Ca may fundamentally change the deformation behavior of Mg, similar to some rare earth elements. Sandlöbes et al. [141] observed an increase in the activity of the <c + a> slip system in Mg-1Al-0.1Ca. According to molecular dynamics (MD) calculations and density functional theory (DFT) calculations, Ca atoms have higher dislocation binding energy and solid solution strengthening on basal <a> slip than on <c + a> slip, and it is predicted that Ca will promote the basal-to-prismatic cross-slip in Mg [142,143].

Reference [135] studied the mechanism of Ca addition on the tensile strain of Mg alloys and specifically analyzed the reason for the increase in plasticity caused by Ca addition. In a tensile test of extruded Mg-0.47 wt.% Ca alloy, the slip activity in the grains was studied under tensile strains of 1%, 2%, 4%, 8% and 16%. Basal slip was the dominant deformation mechanism in this alloy at all strains, whereas prismatic and pyramidal I <a> slips became important after 2% strain. According to Schmid factor analysis, the CRSSs of prismatic slip and pyramidal <a> slip were approximately twice that of basal slip in this Mg-Ca alloy. The enhancement of nonbasal <a> slip activity improved the ductility of the material. The enhanced nonbasal <a> slip activity can be interpreted as Ca reducing the energy barrier for <a> dislocations to cross-slip to nonbasal planes. According to first-principles calculations, solute Ca atoms will reduce the unstable stacking fault energy of all slip modes. The magnesium alloy prepared by SLM also suffered from low plasticity, and some SLMed magnesium alloys have lower plasticity than as-cast magnesium alloys [26,28]. At present, due to the lack of research on the properties of SLMed Mg alloys containing Ca, the improvement in the plasticity of SLMed magnesium alloy provided by Ca alloying still needs to be further studied because of its complex mechanism.

#### 4.1.3. Alloying Element: Sn

Sn is an essential trace element in the human body. Sn can promote the growth and development of the body, break down hemoglobin, and promote tissue growth and wound healing [144]. The chemical properties of Sn are stable [145]. Several studies have shown that the addition of Sn can improve the properties of Mg alloys and that the resulting alloy exhibits excellent mechanical properties and good corrosion resistance, especially when the Sn content is 1 wt.% [145,146]. Zhou et al. [39] investigated the effect of adding different amounts of Sn on the microstructure and properties of SLMed Mg. The addition of Sn will form the  $Mg_2Sn$  phase with Mg. As the Sn content increased, the  $Mg_2Sn$ phase hindered the growth of the grains, the grain size decreased from 25 to 5  $\mu$ m, and the Mg<sub>2</sub>Sn phase increased significantly. On the one hand, the reduction of alloying element segregation during the SLM process and grain refinement slowed the degradation rate. On the other hand, the  $Mg_2Sn$ phase accelerated the degradation rate due to galvanic corrosion. Hence, reducing the degradation rate of SLMed Mg should balance both the grain size and the volume fraction of the Mg<sub>2</sub>Sn phase. The degradation rate of the Mg-Sn alloy was slower than that of Mg when the Sn content was less than 3 wt.%. Grain refinement and segregation reduction were the reasons for this phenomenon. The degradation rate of the alloy increased with increasing Sn content when the Sn content exceeded 3 wt.%. The main reason was that the second phase Mg2Sn caused severe galvanic corrosion and accelerated the degradation of Mg. The corrosion resistance of the Mg alloy was significantly improved when the Sn content was 1 wt.%. In this case, the beneficial effects of grain refinement outweighed the adverse effects of Mg<sub>2</sub>Sn on corrosion resistance [39].

In terms of mechanical properties, Mg had the lowest Vickers hardness (37.9 Hv), whereas Mg-7Sn alloy had the highest Vickers hardness (65.7 Hv) [39]. The hardness of the Mg-Sn alloy increased with increasing Sn content, which was caused by grain refinement and second phase strengthening. The rapid solidification characteristics refined the Mg grains. The hardness of Mg<sub>2</sub>Sn was greater than that of the Mg phase. Therefore, the strengthening of the second phase was due to the presence of

the Mg<sub>2</sub>Sn phase. The discrete Mg<sub>2</sub>Sn phase precipitated at the grain boundaries, which suppressed the motion of dislocations and strengthened the Mg alloy. The introduction of Sn improved the compressive strength of Mg. With increasing Sn content, the compressive strength of the SLMed Mg-Sn alloy increased to 81 MPa (5 wt.%), and as the Sn content continued to increase, the compressive strength of the alloy decreased. The improvement in compressive strength mainly came from grain refinement and Mg<sub>2</sub>Sn phase strengthening. Excessive Sn content led to an increase in the Mg<sub>2</sub>Sn phase. The semicontinuous network of Mg<sub>2</sub>Sn at the grain boundaries accelerated the initiation and propagation of cracks at the phase interface, leading to a reduction in compressive strength. Therefore, the beneficial and harmful effects should be considered comprehensively when introducing alloying elements

## 4.1.4. Alloying Element: Zn

Zinc is one of the most abundant nutritionally essential elements in the human body and has basic safety for biomedical applications [147]. Cai et al. [85] showed that Zn could improve the corrosion resistance and mechanical properties of Mg alloys. The improvement in mechanical performance for Mg-Zn alloys with up to 5 wt.% Zn content corresponds to fine grain strengthening, solid solution strengthening, and second phase strengthening. Polarization tests have shown the beneficial effect of Zn on the formation of a protective film on the surface of alloys. However, adding Zn to Mg will make Mg-Zn binary alloys crack easily during solidification [94]. Therefore, the content of Zn should be controlled within an appropriate range. Yang et al. [148] prepared Mg-Zn alloy by powder metallurgy and pointed out that Mg-Zn alloy is suitable for the human body when the Zn content does not exceed 14.5 wt.%. Boehlert [149] studied Mg-Zn alloys containing 0-4.4 wt.% Zn and found that Zn was a potent grain refiner and strengthener for Mg; moreover, they determined that the optimal Zn content was 4 wt.%. Wei et al. [43] discussed the effect of 1–12 wt.% Zn content on the densification, microstructure and mechanical properties of SLMed Mg-Zn binary alloys. Their results showed that the increase in Zn content had a significantly deteriorating effect on the densification response of the SLMed Mg-Zn alloys. At 1 wt.% Zn content, near full-density products could be obtained. As the Zn content (2–10 wt.%) increased, cracks appeared, which severely affected the relative density of the sample. After the Zn content increased to 12 wt.%, the cracks disappeared, but some micropores appeared, which affected the relative density and mechanical properties of the sample. The mechanical properties of the sample were only improved when the Zn content was 1 wt.%, for which the UTS was 148 MPa and the elongation rate was 11%; these values were similar to those of the as-cast Mg. Zhang et al. [42] asserted that with increasing Zn content, the grain size of SLMed ZK61 magnesium alloy was refined, but the surface quality decreased. The precipitated phases experienced successive transitions:  $MgZn \rightarrow MgZn + Mg_7Zn_3 \rightarrow Mg_7Zn_3$ . With increasing Zn content, the solubility of Zn in the Mg matrix increased. On the basis of the solid solution strengthening theory, high solid solubility will induce excellent properties. In addition, the uniform precipitation of the hard and brittle second phase  $Mg_7Zn_3$  can also promote the mechanical properties. The homogeneously distributed  $Mg_7Zn_3$  phase with higher microhardness could impede the dislocation motion between the grains [150], resulting in increased microhardness. When different manufacturing processes are adopted, the optimal Zn content in the Mg alloy is different. However, it is certain that Zn has a beneficial effect on the properties of SLMed Mg alloys, and the corrosion resistance and mechanical properties of Mg alloys can be improved by grain refinement, solid solution strengthening and precipitation strengthening. When introducing Zn, it is necessary to control the content of Zn and reduce the occurrence of cracking.

#### 4.1.5. Other Regular Elements

Currently, the types of alloying elements introduced in SLMed magnesium alloys are still relatively limited. In traditional manufacturing processes, other alloying elements, such as rare earth elements and Mn, are also introduced to improve the comprehensive performance of as-cast Mg alloys [151,152].

By summarizing the influence of these alloying elements on Mg alloys prepared in the traditional process, more information can be provided for use as a reference for SLMed Mg alloys.

Mg-Mn series alloys are regarded as a new type of Mg alloy that have excellent corrosion resistance, good creep resistance and low cost. The mechanical properties and corrosion resistance of Mg alloys were improved after Mn was introduced [151,153]. Mn addition to Mg-9Al-2Sn alloy led to the formation of Al<sub>8</sub>(Mn, Fe)<sub>5</sub> phases. The formation of Al<sub>8</sub>(Mn, Fe)<sub>5</sub> particles in the interior of grains was likely the reason for grain refinement, which was stable in size during the solution treatment. The addition of 0.1 wt.% Mn had an obvious effect on accelerating the aging behavior of the Mg-9Al-2Sn alloy [151,153]. Adjusting the process parameters can improve the performance of the SLMed magnesium alloy to a certain extent. However, adjusting the process parameters had a relatively limited impact on the performance improvement in SLMed magnesium alloys. In addition to controlling the process conditions, alloying elements must be introduced to further improve the performance of SLMed magnesium alloys. Therefore, it is necessary to introduce more alloying elements and expand the SLMed magnesium alloy series. This is also worthy of attention and research in the future.

In summary, the introduction of alloying elements can play a role in refining the grains and improving the corrosion resistance. However, the amount of the new second phase generated after the introduction of different alloying elements will increase with increasing alloying element content and gradually evolve from discrete precipitation to network precipitation along the grain boundaries, which causes crack initiation and propagation at the second phase/matrix interface, limiting the mechanical properties of the SLMed magnesium alloys. A greater number of alloying elements should be introduced in future research, and additional SLMed magnesium alloy systems should be developed. Additionally, more precise studies are needed to determine the optimal number of alloying elements added to SLMed Mg alloys in order to improve corrosion resistance while minimizing the reduction in mechanical properties.

#### 4.2. Rare Earth Elements

The addition of rare earth elements can reduce the grain size and corrosion current of magnesium alloys, which slows hydrogen evolution and improves corrosion resistance [154]. In general, high nucleation rates and low grain growth rates can lead to the formation of fine grains. In addition, the melting point and the diffusion rate of the atoms may also be related to the grain refining effects of the rare earth addition. It has also been reported that the addition of rare earth elements can remarkably improve the mechanical properties of magnesium alloys by solid solution strengthening and precipitation strengthening [155,156]. Therefore, in the preparation of SLMed magnesium alloy, rare earth elements can be added to improve performance.

Studies have shown that the rare earth element Dy has an effect on the microstructure and corrosion resistance of SLMed Mg-Zn alloys [40]. For the alloys containing 1–5 wt.% Dy, the grain size was significantly refined as the Dy content increased. The main reason for the refinement was that the Mg-Zn-Dy phase had a higher melting point, which reduced the temperature difference between the Mg-Zn-Dy phase and the  $\alpha$ -Mg phase. In the solidification process, the Mg-Zn-Dy phase was formed by the diffusion of atoms within a lower range, and precipitates first formed in the grain boundaries and then  $\alpha$ -Mg solidified. Therefore, the microstructure was effectively refined. Zhang et al. [157] asserted that the addition of rare earth elements reduced the laminar spacing of  $\alpha$ -Mg and that rare earth elements acted as grain refiners. In terms of corrosion resistance, the degradation rate significantly decreased when the Dy content was 1 wt.%. The lowest average hydrogen evolution rate was 0.009 mL cm<sup>-2</sup> h<sup>-1</sup>. When Dy increased to 5 wt.%, the hydrogen evolution rate increased to 0.068 mL cm<sup>-2</sup> h<sup>-1</sup>. When the Dy content was excessive, the abundant heterogeneously distributed Mg-Zn-Dy and MgZn<sub>2</sub> phases might serve as a cathode. However, galvanic coupling with the Mg matrix could accelerate the degradation rate of the alloys. Rare earth elements have a double effect on the degradation rate of SLMed magnesium alloy. On the one hand, rare earth elements can refine the

grains of magnesium alloys and reduce element segregation, thereby reducing the degradation rate of the alloys; on the other hand, a greater amount of the second phase could cause severe galvanic corrosion, which could accelerate the degradation of the Mg alloys. Therefore, the content of rare earth elements should be controlled within an appropriate range. The influence of the rare earth element content and the determination of the optimum rare earth content still need further study.

Due to the lack of literature on the introduction of rare earth elements into SLMed alloys and their related mechanisms, the research results of the influence of rare earth elements on magnesium alloys produced by the traditional process can be used for reference. In a traditional preparation, Li et al. [158] studied the influence of the rare earth elements Sm and La on the microstructure and mechanical properties of as-cast Mg alloys. The Mg-0.5Zn-0.2Mn-0.2Sm/0.3La-0.4Ca alloy exhibited good ductility with A (elongation) values of 27.5-30.5%, whereas the Mg-0.5Zn-0.2Mn-0.2Sm-0.3La alloy exhibited an excellent balance of strength and ductility with an Rp0.2 (UTS) value of 190 MPa, an Rm (high YS) value of 239 MPa, and an A (elongation) value of 23.9%. After the introduction of Sm and La, the grains were refined by the segregated atoms at the head of the solid-liquid solidification and the aggregated particles near the grain boundaries. Moreover, Sm and La helped weaken the texture, thereby improving the plasticity. The weakened texture with the addition of rare earth elements was due to the dynamic recrystallization (DRX) and the weakened dynamic recrystallized (DRXed) texture. Yamasaki et al. [159] studied the influence of Gd on the mechanical properties of Mg alloys. The Mg-Zn-Gd alloy exhibited high strength (345 MPa) and large elongation (6.9%) due to the refinement of  $\alpha$ -Mg grains and the existence of a highly dispersed hard long-period ordered (LPO) structural phase. The LPO phase was also found in the Mg-Zn-Y alloy system [160]. The 18R-type long-period stacking (LPS) phase had a higher hardness than the Mg matrix phase. The most essential characteristic in the microstructures of these Mg-Zn alloys containing rare earth elements (denoted Mg-Zn-RE alloys hereinafter) was a long-period stacking ordered (LPSO) structural phase. The mechanical properties and corrosion resistance of Mg-Zn-RE alloys containing the LPSO phase can be improved by rapid solidification [92]. In the solidification process of Mg alloys, the change in cooling rate had a great influence on the corrosion behavior of Mg-Zn-Y alloys. The rapid solidification technology improved the microstructure and electrochemical uniformity of the Mg-Zn-Y alloys, leading to the passivation of the matrix material. The optimum cooling rate of the Mg-Zn-Y alloys was  $3 \times 10^4$  K s<sup>-1</sup>. The cooling rate was slow, and a large number of LPSO phases were formed in the casting process, which deteriorated the corrosion resistance. The increase in cooling rate led to a delay in the occurrence of filamentous corrosion. This was due to the grain refinement in the alloy and the formation of the supersaturated single  $\alpha$ -Mg phase solid solution [92].

To date, most reported biomedical magnesium alloys contain rare earth elements. In the application of rare earth elements, attention should be paid to the toxic effects of rare earth elements. Rare earth elements may induce latent toxic and harmful effects on the human body [161,162]. Consequently, alloying elements must be chosen with careful consideration of the possible toxic effects.

Studies on introducing rare earth elements into SLMed alloys are still lacking. Future studies in this area can refer to studies on the addition of rare earth elements in magnesium alloys produced by other forming processes. Combined with the advantages of rapid solidification in the SLM process and the extension of the alloying system used in the SLMed magnesium alloy, it is necessary to explore the influence of the content of rare earth elements on the properties of SLMed magnesium alloys and determine the optimal rare earth element content. However, it is also important to consider the toxicity of rare earth elements in the biological field.

## 5. Microstructure of SLMed Magnesium Alloy

Because SLM has the characteristics of rapid solidification, the cooling rate can reach  $10^4-10^5$  K·s<sup>-1</sup>. The microstructure varied with respect to variations in the cooling rate. The microstructures in the as-cast, sub-rapidly solidified, and rapidly solidified (i.e., SLMed) samples can be compared under different cooling rates.

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Figure 15a,b are optical microscopy and SEM images of the as-cast AZ61 alloy [163]. The as-cast alloy exhibited a typical dendritic eutectic network structure. The phase composition in the as-cast AZ61 was composed of an  $\alpha$ -Mg matrix and a  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> eutectic phase distributed in grain boundaries and grains. The average grain size of the as-cast AZ61 alloy was approximately 320 ± 5 µm. Under normal conditions, the grains were coarse and non-uniform. The microstructure of as-cast AZ91D is shown in Figure 16a,b. As-cast AZ91 also consisted of an  $\alpha$ -Mg solid solution and a  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> eutectic phase. As shown in the enlarged micrograph of area A (Figure 16b), some of the divorced eutectic  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> was surrounded by lamellar eutectic. In the die-cast AZ91D ingot,  $\beta$  precipitates existed in the form of partially divorced eutectic structures. AZ61 and AZ91D are hypoeutectic magnesium aluminum alloys with low zinc content. In hypoeutectic Mg-Al alloys, the morphology of the eutectic phase depends on the cooling rate. A higher cooling rate resulted in a more discrete microstructure [164]. Therefore, the inherently high cooling rate in the SLM process caused a change in  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> between the SLMed part and the as-cast part of Mg alloy. For die-cast samples, most of the Al and Zn were concentrated in the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase [165]. The reduction in the Al content in the  $\alpha$ -Mg solid solution not only reduced the effect of solid solution strengthening but also deteriorated the corrosion behavior.

Sub-rapid solidification is a nonequilibrium solidification process with a solidification rate of  $10^3$  K/s [69]. The sub-rapidly solidified structure changed considerably from that of the as-cast sample (Figure 15c). The  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase continuously distributed on the grain boundaries disappeared. The microstructure was obviously refined and was mainly composed of small equiaxed grains. The literature noted that as the thickness of the sheet decreased (i.e., the faster the solidification process), the grain size decreased [72], and a large number of petal-like dendrites appeared in the microstructure. Owing to the high cooling rate, the dendrite structure was very small, so it was difficult to distinguish the dendrite arm spacing in the low-magnification metallographic microstructure. Under sub-rapid solidification, the grain size of the AZ61 magnesium alloy was 13.5 µm, which was much smaller than that of the as-cast AZ61 magnesium alloy.

The solidification rate of SLM was faster than that of sub-rapid solidification. As shown in Figure 15d, the SLMed microstructure was more uniform, the  $\alpha$ -Mg grains were refined and equiaxed, and the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase precipitated at the grain boundaries. The  $\alpha$ -Mg crystal grains and  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> in the SLMed microstructure were more refined than those in the sub-rapidly solidified microstructures. The grain size in Figure 15d was 2.46 µm (at an energy density of 208 J/mm<sup>3</sup>). Other studies have also found the same microstructural characteristics of SLMed magnesium alloys [26,29,30]. Wei et al. [26] investigated the distribution of Mg and Al in SLMed AZ91D samples. Comparing the SLMed samples with as-cast AZ91D, the distribution of Mg and Al in the SLMed AZ91D was more uniform, and the content of Al in the matrix varied with respect to the energy density. This finding demonstrates that the chemical composition distribution was more uniform under rapid solidification, which is beneficial to reduce the segregation of the components, and the energy input has an effect on the solid solution [166].

The rapid solidification of SLM mainly affects the generation of the second phase in the alloy. Cai et al. [167] compared the microstructure and morphology of the second phase  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> in the conventional as-cast part and in the part produced under rapid solidification. Compared with conventional casting,  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> in the rapidly solidified AZ91 magnesium alloy had smaller and fewer micropores. The dispersive microporosity will act as crack initiation sites and promote crack propagation under the application of an external force, causing significant deterioration in tensile properties. These micropores were mainly formed by solidification shrinkage and dissolved gas. Liu et al. [28] compared the microstructures under different energy densities under SLM and found that as the energy density increased, the microstructure changed. When the energy density was low, the precipitated second phase gradually precipitated along the grain boundaries, and the grain size slightly increased. Other studies noted that the solid solution was related to the energy input. As the energy input increased, the solid solution of the elements and the precipitation of the second

phase were both related to the energy input and solute capture. Therefore, analysis and discussion need to be combined with the solidification path.



**Figure 15.** Microstructure of AZ61: (**a**,**b**) as-cast AZ61. Reproduction from [163], with permission fromElsevier, 2020. (**c**) Sub-rapidly solidified AZ61. Reproduction from [72], with permission from Elsevier, 2020. (**d**) SLMed AZ61. Reproduction from [28], with permission from Elsevier, 2020.



**Figure 16.** Microstructure of as-cast AZ91. (**a**) microscope picture; (**b**) SEM picture. Reproduction from [26], with permission from Elsevier, 2020.

In Figure 17, the left diagram is the phase diagram of the Mg-Al binary system [168], whereas the right diagram is the phase diagram of the AZ61 Mg alloy [28]. The addition of Zn obviously had a greater impact on the Mg-Al binary system phase diagram. Analysis of the equilibrium cooling process of AZ61 shows that the solidification path of the red line in the figure was  $L \rightarrow L + \alpha$ -Mg  $\rightarrow \alpha$ -Mg  $\rightarrow \alpha$ -Mg  $+ \beta$ -Mg<sub>17</sub>Al<sub>12</sub>  $\rightarrow \alpha$ -Mg  $+ \beta$ -Mg<sub>17</sub>Al<sub>12</sub> + T.



**Figure 17.** Mg-Al alloy equilibrium phase diagram: (a) Mg-Al binary system. Reproduction from [168], with permission from Elsevier, 2020. (b) AZ61 (1.27% Zn). Reproduction from [28], with permission from Elsevier, 2020.

Taking the AZ series Mg alloy as an example, the maximum solubility of Al in Mg was 12.7 wt.% at 437 °C during equilibrium solidification, whereas the solubility of Al was only 2 wt.% at room temperature. The reaction  $L \rightarrow \alpha$ -Mg occurred first under slow cooling. The Al atoms diffused sufficiently, and the alloy composition in  $\alpha$ -Mg gradually became uniform. As the cooling process progressed, the reaction  $L \rightarrow \alpha$ -Mg ended when the melt temperature dropped to the solid phase line. Subsequently, the second phase  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> began to precipitate in the  $\alpha$ -Mg solid solution, and the final solidified products in the equilibrium state were  $\alpha$ -Mg solid solution and the second phase  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub>, and there was no eutectic phase. However, SLM is a nonequilibrium process under rapid solidification, so the final phase composition of the SLMed part was slightly different from the equilibrium phase diagram. The AZ61 Mg alloy was composed of two phases of  $\alpha$ -Mg and  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> at room temperature during a relatively slow cooling process. At a faster cooling rate (higher scanning speed and lower laser power), the atoms in the primary  $\alpha$ -Mg in the liquid phase did not have time to diffuse sufficiently. From the principle of solute redistribution, it is known that the solid solution of Al was continuously enriched at the solidification front, and the residual liquid phase between the dendrites of the  $\alpha$ -Mg reached the eutectic composition in the late solidification period. The two phases grew independently to form a divorced eutectic structure. As a result, the temperature of the molten pool was low, and the cooling rate as fast at low energy input (138.89 J/mm<sup>3</sup>), which is equivalent to being extremely cold in the  $\alpha$ -Mg region. Due to the lack of sufficient diffusion time, Al dissolved into the matrix. The solid solution of Al in the matrix increased. Hence, the eutectic transformation process L  $\rightarrow \alpha$ -Mg +  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> was suppressed. The precipitation of  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> was less prominent at low energy input. In contrast, due to the accumulation of heat and the decrease in the solidification speed, the solute capture effect was weakened when the energy input was high (156.25–208.33 J/mm<sup>3</sup>). Al diffused more fully, the content of solid solution elements decreased with increasing *Ev*, the eutectic transformation  $L \rightarrow \alpha$ -Mg +  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> occurred, and the crystallinity of  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> increased.

The change of microstructure (grain shape, size, second phase distribution) is related to the cooling rate. As expected, various laser parameters resulted in different solidification rates of the molten pool and thermal cycles, leading to variation in microstructures of the melted zone. In the SLM process, the combination of scanning speed and laser power is the key to controlling the cooling rate. In addition, the faster the cooling rate, the finer the microstructure; the lower the cooling rate during solidification, the longer the time available for grain coarsening. Generally speaking, as the scanning speed decreases and the laser power increases (that is, the line energy density increases), the accumulation of heat in the molten pool causes the temperature of the molten pool to rise, the cooling rate slows down, and the grain size gradually becomes coarser [35]. The increase of the laser power or decrease of the laser scanning speed led to the coarsening of the grains in the melted zone because the higher laser

power or slower laser scanning speed provided more driving force for grain boundary movement, which then promoted the growth of grains. At lower scanning speeds, the prolonged interaction time between the laser and the powder suppresses the heat dissipation in the molten pool. Therefore, due to the larger heat accumulation, the epitaxial growth kinetic conditions of the grains are enhanced [16]. Similar results were obtained for pulsed laser samples. When the laser power was low or the scanning speed was high, the average gain size became small, since decreasing the laser power in effect acts in the same way as reducing the preheat temperature of the powder when the next pulse hits the base. The relatively high cooling rate at low laser power or high laser scanning speed restrained the growth of  $\alpha$ -Mg grain during solidification.

As the line energy density increases (low scanning speed and high laser power), the microstructure follows the evolution of clustered finer dendrites-refined equiaxed grains-coarsened equiaxed grains [26,28]. The grain size of AZ61 magnesium alloy can be refined to 1.61  $\mu$ m ( $E_v$  = 138.89 J/mm<sup>3</sup>). Then, the grains changed to an equiaxed shaped (1.79 µm) with an increase in laser energy input to 156 J/mm<sup>3</sup>. Further increase in the laser energy input to 178 J/mm<sup>3</sup> and 208 J/mm<sup>3</sup>, equiaxed grains of 2.12 µm and 2.46 µm, respectively [28]. This is due to the decrease in cooling rate caused by changes in scanning speed and laser power and accumulation of heat in the molten pool. This same reason can explain the change of the grain size far from the center of the molten pool. The  $\alpha$ -Mg grains inside the molten pool show equiaxed crystal morphologies. On the contrary, with the farther away from the molten pool, the  $\alpha$ -Mg grains show a transformation from equiaxed crystal to columnar crystal and the grain size increases [38]. The ratio G/R of the temperature gradient (G) and the solidification rate (R: the propulsion rate of the solidification interface in the normal direction) in the crystal direction of the pulsed light spot determines the microstructure morphology after solidification. Inside the molten pool, G is very high, but R tends to 0, so that the value of G/R is high, which causes the solidification structure to be equiaxed crystal. Further away from the molten pool, G decreases but R gradually increases, so that the value of G/R gradually decreases. The influence of scanning speed and laser power on the precipitation of the second phase has been described in detail above.

Consequently, the grain size, the second phase precipitation, and the element solid solution can be achieved by controlling the process parameters, i.e., controlling the scanning speed and laser power (energy density). In terms of grain size, by comparing the microstructure of magnesium alloys at different cooling rates, it can be seen that faster cooling rates are beneficial for refining the microstructure. From the as-cast state to sub-rapid solidification and rapid solidification (SLM), the grain size of the magnesium alloy drops from  $\sim$ 320  $\mu$ m to  $\sim$ 2  $\mu$ m, which is a change of two orders of magnitude. Properly increasing the scanning speed and lowering the laser power (i.e., lowering the energy density) is beneficial for the improvement of the cooling rate and the reduction of heat accumulation in the molten pool, thereby refining the microstructure. In terms of second phase precipitation, the increase of the cooling rate is beneficial to suppress the occurrence of the phase transition L  $\rightarrow \alpha$ -Mg +  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> and the precipitation of the second phase is reduced. In addition, the energy density must be controlled within a suitable range. Too high an energy input will lead to coarse grains, an increase in element segregation and a decrease in the solid solution. However, if the laser power is reduced or the scanning speed is increased blindly (too low an energy density), the powder cannot be fully melted and combined, thus causing serious pores and affecting the sample quality. Therefore, further research must be performed to more accurately control the solidification structure by controlling scanning speed or laser power and the effect of the solidification structure on the defects and mechanical properties of SLMed magnesium alloys.

#### 6. Effect of Heat Treatment on SLMed Magnesium Alloy

## 6.1. HIP

Some performance breakthroughs have been achieved in SLMed magnesium alloy, but there are still some problems, such as porosity and low elongation. Defects in the sample can be improved by

adjusting the process parameters to improve the fusion of the powder. On the other hand, the pores caused by thermal convection in the molten pool are difficult to remove, requiring the introduction of post-treatment processes, such as HIP. The mechanism of HIP is to apply temperature and pressure to the sample at the same time and hold it for a certain time so that the sample is densified during the pressurization process after heating to eliminate the internal pores. There are some studies on collapsing the pores of SLMed parts by HIP [169–171].

According to the literature [172], the strength properties of SLMed samples are considerably inferior to those of the alloy consolidated using HIP technology, suggesting that it is reasonable to expose the complex-shaped SLMed workpieces to additional HIP treatment. Liu et al. [41] believed that the plasticity of the SLMed AZ61 magnesium alloy was greatly improved after 3 h of HIP at 450 °C and 103 MPa. The results showed that the elongation reached 8.2%, the UTS of the material remained unchanged, the elongation increased (160% greater than that of the SLMed part without HIP), and the plasticity was greatly improved. The improvement in plasticity mainly came from the following two parts: the reduction in the original defects (pores) in the SLMed magnesium alloy and the solid solution of the second phase  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub>. The temperature of the SLMed AZ61 part increased below the melting point during HIP, the magnesium alloy softened and then gradually densified under pressure, eventually eliminating the internal pores, and the density was close to 100%. The elongation was related to the distribution of the second phase. The temperature during HIP was slightly higher than the solidus temperature. As a result, the second phase dissolved into the matrix, which greatly reduced the source of cracks at the interface between the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> and  $\alpha$ -Mg phases. It can be seen that densification and solution treatment are beneficial to improving the plastic elongation of SLMed magnesium alloys.

However, HIP can also adversely affect certain mechanical properties of magnesium alloys. The YS of SLMed magnesium alloys decreased as the grain size increased [41]. Moreover, for SLMed aluminum alloys, HIP post-treatment can have an adverse effect on grain size [173]. HIP postprocessing can lead to grain growth in certain coarser grained areas, probably due to a local imbalance between driving and dragging forces, which corresponds to higher defect density and fewer pinning precipitates. This is a problem that can be solved by appropriately reducing the temperature or shortening the holding time. HIP experiments can verify that the second phase solid solution plays a positive role in improving the plasticity of magnesium alloys. Moreover, the second phase had an impact on the corrosion resistance [174,175]. HIP is a comprehensive heat treatment process that includes closing pores and providing internal heat treatment. Magnesium alloys are affected by the combined effects of temperature, pressure and holding time during HIP, which affect the pores and microstructure. Therefore, different magnesium alloys require different processing parameters, and there is still a lack of experimental data to support the selection of appropriate processing parameters. Hence, more exploration will be needed in order to accurately select the HIP parameters.

#### 6.2. Heat Treatment

Reducing or eliminating the effect of the second phase on the properties of magnesium alloys can also be achieved by heat treatment and other methods. Common magnesium alloy heat treatment methods include solid solution heat treatment (T4), aging heat treatment (T5), and solid solution + aging heat treatment (T6). SLMed magnesium alloy has the problem of poor plasticity, which can be improved by introducing an appropriate heat treatment process.

In AZ series Mg alloys, the presence of the  $\beta$ -phase influences the corrosion behavior to a great extent. The machinability of Mg alloys is also influenced by the amount and distribution of the  $\beta$ -phase. In materials engineering, heat treatment is a promising technique to alter the microstructure to achieve the desired phases and corresponding volume fractions in order to alter the bulk behavior. Chowdary et al. [176] noted that heat treatment of AZ91 Mg alloy greatly affected the amount and distribution of the secondary phase at the grain boundaries and asserted that the machinability of AZ91 Mg alloys can be improved by developing supersaturated grains and reducing the amount of

the secondary phase. The corrosion resistance was greatly affected after the heat treatment due to the supersaturated grains, which promoted a higher corrosion rate [176]. The literature [177] showed that the elongation increased from 7.4 to 11.2% in an as-cast magnesium alloy after T4 heat treatment. T4 treatment (solid solution) significantly improved ductility but reduced YS. T6 (solution + aging) increased the UTS but reduces the YS and ductility.

Wang et al. [177] proposed a new heat treatment idea: solution treatment at 413 °C caused the  $\beta$  phase to dissolve into the matrix. In contrast, the design purpose of Tx is to break the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase network, provide better ductility in exchange for a slight decrease in strength, and comprehensively improve strength and elongation. Treatment at a temperature close to the solvus, typically at 365 °C for just 2 h according to the equilibrium phase diagram, caused the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase to dissolve partially, and the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> network was effectively broken up. This resulted in a composite structure that, with the exception of a few primary  $\alpha$ -Mg globules, consisted of fine  $\alpha$ -grains and the fine remaining  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub>-grains located along the grain boundaries, mainly at the triple grain boundary junctions. If the heat treatment temperature was set to Tx, rather than T4, T5 or T6, both strength and elongation can be improved.

In the literature [178], the solution treatment dissolved the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase and coarsened the grains. During the aging process, the  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> phase preferentially and discontinuously precipitated at the grain boundaries, and then a continuous precipitated phase appeared inside the grains. Both the strength and the elongation were improved after solution treatment and aging treatment. Annealing dissolved  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> and increased the concentration of Al solute in the matrix, which effectively reduced the damping capacity. Mg<sub>17</sub>Al<sub>12</sub> distributed on the grain boundaries also caused local intergranular cracking.

Jia et al. [179] performed a solution heat treatment on Mg-Zn alloys. The enhancement of UTS was due to the solution strength effects of the alloying elements. In addition, Zn dissolving into the Mg matrix decreased the stacking fault energy of the matrix, which led to a change in the plastic deformation mechanism. Thus, the solution treatment enhanced the UTS and elongation simultaneously. The corrosion resistance of the solution-treated samples was superior to that of the as-cast samples.

It can be seen that heat treatment plays a positive role in improving the strength, plasticity, and corrosion resistance of magnesium alloys. However, there is still a lack of attention in the post-treatment of SLMed magnesium alloys. For the inherent defects in SLMed samples, such as pores, it is necessary to introduce postprocessing steps to eliminate them. Comprehensive improvements in the mechanical properties and corrosion resistance of SLMed magnesium alloys can be considered by adding heat treatment. However, it is necessary to further explore the optimal postprocessing parameters to control the adverse effects of grain size growth on the properties of magnesium alloys to balance the effects of grain size and microstructure.

## 7. Outlook

The development of SLM of magnesium alloys has been reviewed, and an extensive analysis of the available literature on the preparation of metals via SLM has led to the recognition of the influential process parameters and material properties. At present, the limited processable materials, immature process conditions and metallurgical defects restrict the development and application of SLMed magnesium alloys. Some efforts have been made to solve the above problems, such as adding alloy elements and applying postprocessing. However, the breakthroughs of SLMed magnesium alloys in these two areas have not been reviewed. Therefore, this article gives an overview of these three issues. In this paper, the process parameters, alloying elements, microstructure, properties, and postprocessing steps were systematically summarized. For the purpose of high efficiency, high quality, low cost, and more stable use of SLM to prepare high-performance magnesium alloys, scholars have carried out research on process parameters, alloying elements, and post-treatment steps. Although some progress has been made in terms of the relative density, mechanical properties, and corrosion resistance of magnesium alloys, the literature is still limited to unsystematic performance studies of a few types of magnesium alloys. Hence, current SLMed parts are produced under suboptimal process conditions, wherein it is difficult to control metallurgical defects.

In the future, there are still several issues that need attention in the manufacturing of magnesium alloys via SLM.

First of all, in view of the lack of processable materials, in order to expand more processable SLMed magnesium alloy materials and improve the problem of limited processable materials, we reviewed the progress of SLMed magnesium alloys in the addition of alloying elements, but there are still two problems in this area: the types of added alloying elements are limited, and the research of the addition of alloying elements needs to be in-depth. At present, most studies on SLM fabrication of magnesium alloys focus on the influence of process parameters and simple alloying elements on the microstructure and properties of binary alloys. Aside from research on Mg-Al-Zn alloys, Mg-Zn-Zr alloys, and Mg-Zn alloys, few studies have been reported on other as-cast Mg alloys and wrought Mg alloys, especially the high-strength and highly corrosion-resistant Mg alloys that are in great demand in the aerospace field (e.g., Mg-Mn alloys). We also combined the relevant research on the mature alloy element addition route in the traditional process to provide a reference for the alloy design of SLMed magnesium alloys, such as Mn and Ca, and the addition of these elements in SLMed magnesium alloys has rarely been reported. Therefore, there is a need to broaden the scope of the applicable magnesium alloys for SLM and design new materials whose compositions are suitable for the process characteristics of laser AM. In addition, post-treatment can also be applied to improve the machinability of magnesium alloys in the SLM process. We reviewed the current research progress in the postprocessing part, and the results showed that the post-processing can effectively improve the properties of SLM magnesium alloys, especially to improve the plasticity, but there are few studies at present, which is an area that needs to be further studied in the future. Traditional preparation techniques of magnesium alloys are also evaluated and related to the SLM process with a view to gaining useful insights especially with respect to postprocessing.

Second, in view of the immature process conditions, we comprehensively reviewed the new progress of different magnesium alloy materials in SLM process conditions and forming, and combined process conditions with relative density, grain size, microstructure, mechanical properties, and corrosion resistance. In the review of microstructure, the microstructure under different preparation processes (different cooling rates) was compared longitudinally, and the microstructure under different process conditions in the SLM process was also compared horizontally. In addition, it is different from the previous reviews of SLMed magnesium alloy.

Third, in terms of metallurgical defects, defects such as oxidation and cracks are reviewed. Research on cracks has made progress recently, but there is lack of review of the latest research on cracks. Cracks are a serious defect that limits the application of magnesium alloys and leads to premature failure of materials. Therefore, it is necessary to review the research progress of SLMed magnesium alloy cracks. It is well known that the application of SLMed Al alloy has been limited by cracks, so the paper combines the research progress of SLMed Al alloys on cracks to provide more references for the research of SLMed magnesium alloy cracks. In terms of oxidation, inspired by the purity of molten steel, this review not only looks forward to the development of SLMed magnesium alloys from the perspective of materials and processing, but also considers the future improvement direction of SLMed magnesium alloys from a new perspective—a metallurgical perspective. In addition, this was mentioned in the previous review of SLMed magnesium alloys. In research on steel materials, the harmful effect of nonmetallic inclusions on steel properties has been widely recognized [180,181]. For bearing steel, the deoxidation and purification of liquid steel has always been the focus of attention. Research has found that when the total oxygen content in molten steel is reduced from 0.0026 to 0.001%, the fatigue life of bearing steel is increased by a factor of 10, and when the total oxygen content is reduced from 0.001 to 0.0004%, the fatigue life is increased by an additional factor of 10. Therefore, to improve the performance of steel materials, it is important is to minimize both the dissolved oxygen

in liquid steel and the content of oxide inclusions generated during the solidification process [182,183]. There have been many studies on the harmful effects of high oxygen content on material properties in powder metallurgy, such as 718 alloy [104], Al alloy [103], and titanium alloy [184]. Due to the highly oxyphilic nature of magnesium, the oxygen inevitably enters the magnesium alloy base metal and the magnesium alloy powder during the preparation process. However, the amount of oxygen entering the alloy system at various stages, the size and number of oxide inclusions formed in the alloy, and the mechanism of the influence of inclusions on the alloy—especially the influence of inclusions in the performance of magnesium alloys—have rarely been studied. Currently available research is limited to the understanding of the oxide film in the SLM process. It was found that the oxide film is usually located at the top of the molten pool, and the oxide film on the surface will affect the wettability, thereby weakening the interlayer bonding and resulting in the formation of defects. Improving the oxidation also means reducing the defects in the material. It was found that the use of a high-power laser could break the oxide film on the surface, but this increased the burning loss of alloying elements, and balancing the contradiction between these two aspects is a new topic. From the perspective of the preparation process of magnesium alloys, the oxygen that can enter into the alloy mainly comes from the mold cavity and the powder preparation process as well as the smelting of the magnesium base material. Future studies should focus on methods to inhibit the entry of oxygen in these processes and the mechanism of the influence of a small amount of oxygen on SLMed magnesium alloy materials.

In the future, the physical and chemical reactions in the SLMed magnesium alloy process need to be studied theoretically, especially the thermodynamics and kinetics of the formation of intermetallic compounds. For example, the thermodynamic calculation of the enthalpy of fusion of SLMed magnesium alloys with different compositions can theoretically determine the energy required for the magnesium alloy powder of a specific composition, which provides a theoretical basis for setting the laser power for actual experimental production (i.e., this approach can help ensure that the powder is melted under the optimal energy setting). In terms of dynamics research, it is necessary to establish a model of the relationship between the expansion and solidification of magnesium melt to seek the optimal energy input, control the melt temperature, and obtain the relationship between magnesium melt spreading and solidification rate to reduce the occurrence of defects, such as pores and spheroidization.

Furthermore, the influence of intermetallic compounds on SLMed magnesium alloys cannot be ignored. Intermetallic compounds have a dual effect on SLMed magnesium alloys. On the one hand, refining and dispersing intermetallic compounds can play a role in precipitation strengthening; on the other hand, intermetallic compounds can also have an adverse effect on corrosion resistance and mechanical properties. Therefore, controlling the size, shape and content of intermetallic compounds should be studied in further detail in the future. It is necessary to proceed from the theory of metallurgical physical chemistry and seek the conditions and mechanisms for the formation or decomposition of intermetallic compounds from the liquid state to the normal temperature state and finally obtain the best process parameters for controlling the intermetallic compounds in the SLM process, including an appropriate heat treatment method. According to the theoretical basis of postprocessing SLMed magnesium alloys presented above, there is still much research space in this aspect.

#### 8. Conclusions

This review of the published literature on SLMed Mg offers insight into the current knowledge surrounding the influence of processing conditions, alloying elements, and post-treatment on the microstructure, properties, and fracture mechanisms of the produced parts. However, limited processable materials, immature process conditions and metallurgical defects are still problems that magnesium alloys need to face and solve in the SLM process. In the past two years, these three issues of SLMed magnesium alloys have been substantially improved by optimizing process parameters, introducing post treatment and adjusting different alloying elements. Due to the paucity of publications

on postprocessing and alloy design of SLMed magnesium alloy powders, we review the current state of research and progress. Moreover, traditional preparation techniques of magnesium alloys are evaluated and related to the SLM process with a view to gaining useful insights especially with respect to postprocessing and alloy design of magnesium alloys. This article also discusses and summarizes the current factors that affect the formability, compactness, and mechanical properties of SLMed magnesium alloys. This article provides a reference for further investigating or controlling the microstructure of SLMed magnesium alloys and improving the densification, mechanical properties, and corrosion resistance of the produced materials. In addition, with respect to materials and metallurgy, new challenges and prospects in the SLM processing of magnesium alloy powders are proposed with respect to alloy design, base material purification, inclusion control and theoretical calculation, and the role of intermetallic compounds.

- With respect to immature process conditions and metallurgical defects, the influence of processing parameters (scanning speed and laser power) on the forming and performance of magnesium alloys cannot be ignored. The relative density of magnesium alloys is closely related to the processing parameters. If the scanning speed is too high or laser power is to low (energy density is too low), the powder cannot be fully melted, and the system is in a state of solid–liquid coexistence. In this state, the surface tension and viscosity of the liquid increase, which inhibits the liquid from flowing smoothly and causing the liquid to agglomerate into spheres and pores, thereby preventing the sample from becoming dense. If the energy density is too high, it will lead to the loss of alloying elements due to the evaporation of elements in the powder. On the other hand, under these conditions, the solute capture effect will be weakened, and the decrease in the solid solution content will cause the relative density of the SLMed sample to decrease. Therefore, the preparation of dense SLMed magnesium alloy requires the energy density to be controlled in a suitable range to enhance the solid solution strengthening and reduce the liquid surface tension, thereby eliminating the pores and spherical particles between the tracks. However, in the SLM process of magnesium alloys, it is difficult to remove the pores by only adjusting the process conditions. Post-treatment methods such as HIP are required to remove these defects. Microcracks are commonly attributed to solidification cracking and liquation cracking. The cause of solidification cracking is a residual thin film of liquid phase between the primary crystallized grains, and liquation cracking is caused by cyclic heat input, which occurs in multilayer welding and layered fabrication.
- The microhardness of the SLMed magnesium alloy is affected by the rapid solidification characteristics in the SLM process, which mainly affect the microstructure and the solid solution of the elements. On the one hand, the rapid solidification characteristics remarkably refine the microstructure of magnesium alloys, and the microhardness of SLMed magnesium alloys is notably higher than that of traditional as-cast magnesium alloys. On the other hand, the solid solution content of the alloying elements is different due to the differences in the solute trapping effects at different energy densities during the SLM process; thus, the strengthening effects are different. Moreover, the distribution and content of the second phase and the presence of defects will also affect the microhardness. Microhardness does not change monotonically with respect to the energy density. It is necessary to comprehensively consider the interaction between the solute capture effect at different molten pool temperatures and the solid solution of the elements under rapid solidification. Hence, while the microstructure is refined, the optimal solid solution is achieved, and the microhardness of the magnesium alloy is improved.
- The grain size of magnesium alloys is increased by increasing the energy input during the SLM process, and the mechanical properties are affected by the grain size and microstructure. In SLMed magnesium alloys, attention should be paid to the dual influence of the second phase on the material properties. The content of the second phase needs to be controlled to balance the strengthening of the second phase and its limitation on plasticity. The mechanical properties and corrosion resistance of SLMed magnesium alloy can be improved by introducing alloying elements.

At present, there are several alloy systems under investigation, and more alloying elements, such as rare earth elements and Mn, need to be introduced to develop different SLMed magnesium alloy systems. The micropores and the second phase generated during the SLM process have certain restrictions on the application of the material. Adjusting the process conditions can reduce the harm of the pores and the second phase to a certain extent, but it cannot be completely avoided. Post-treatments, such as HIP and heat treatment, can be applied to help eliminate inherent porosity and improve the precipitation of the second phase. However, much remains to be done in this area.

In view of the lack of processable materials, adding alloying elements and post-treatment is an
effective way to improve SLMed magnesium alloy. These two methods have played an important
role in improving the mechanical properties and corrosion resistance of SLMed magnesium alloy,
especially the problem of poor plasticity of SLMed magnesium alloy. In the future, these two
aspects need to be further studied to design magnesium alloy materials that are more suitable for
SLM process applications.

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