

Article

The Activation of Magnesium Sintering by Zinc Addition

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Abstract: Light alloys based on magnesium are widely used in most areas of science and technology. However, magnesium powder alloys are quite difficult to sinter due to the stable film of oxides that counteracts diffusion. Therefore, finding a method to activate magnesium sintering is urgent. This study examines the effect of adding 5 wt. % and 10 wt. % zinc to the sintering pattern of magnesium powders at 430 °C; a dwell of 30 min was used to homogenize at the densification's temperature. Scanning electron microscopy (SEM) was used to characterize the alloy's microstructure, while the phase composition was characterized using X-ray diffraction (XRD) and energy dispersion spectroscopy (EDS). The sintering densities of Mg–5Zn and Mg–10Zn were found to be 88% and 92%, respectively. The results show that after sintering, a heterophase structure of the alloy is formed based on a solid solution and phases MgZn and Mg₅₀Zn₂₁. To establish the sintering mechanism, the interaction at the MgO and Zn melt phase interface was analyzed using the sessile drop method. The minimum contact angle—65°—was discovered at 500 °C with a 20 min holding time. It was demonstrated that the sintering process in the Mg–Zn system proceeds through the following stages: (1) penetration of zinc into oxide-free surfaces; (2) crystallization of a solid solution, intermetallics; and (3) the removal of magnesium oxide from the particle surface, with oxide particles deposited on the surface of the sample.

Keywords: magnesium; powder metallurgy; sintering; magnesium alloying



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1. Introduction

Magnesium (Mg) and its alloys are widely used to design and manufacture low-weight structural parts for the automotive, nuclear reactor, and aerospace industries [1,2]. Mg also attracts particular attention from bioengineers as a potential material for bioresorbable implants [3]. In general, magnesium alloys were prepared by casting methods [4]. However, several problems are encountered during magnesium melting and casting [5]. The primary issues affecting casting quality, such as porosity and low dimensional accuracy, stem from magnesium's high affinity for oxygen. Casting must be implemented using different fluxes and gases to prevent the rapid oxidation and burning of magnesium. An alternative way to produce magnesium-based products is powder metallurgy. This technology allows for the precise control of the chemical composition, high precision tolerance, and manufacturing of parts without melting. Yunpeng Zhu et al. [6] consolidated the magnesium alloy AZ91 by spark-plasma sintering (SPS). To prevent the influence of oxide layers on mechanical properties, the authors propose the creation of a random texture in material and quenching. Furthermore, Bartomiej Hrapkowicz et al. [7] showed the possibility of preparing the Mg–Zn–Ca–Pr alloy by high-energy milling (HEM) and sintering via SPS. During HEM, a solid solution based on Mg, MgZn₂, Ca_{4.05}Mg_{13.85}Zn_{28.10} was formed that resulted in high hardness (230–373 HV0.05) and bending strength (123–193 MPa). Many studies [8–11] have been devoted to the production of magnesium alloys using the SPS method, but

a common disadvantage includes the preservation of magnesium oxide on the surface of the particles, which significantly reduces tensile strength [12]. One of the ways to neutralize the influence of Mg oxide is through activating sintering. In the fundamental works of Martin Wolff et al. [13,14], it was shown that the activation of the sintering process can be achieved by adding a small amount of calcium (Ca). Calcium additions protect magnesium particles against oxygen diffusion and can reduce MgO layers. At temperatures between 445 and 517 °C, liquid phase sintering is possible, depending on the calcium concentration. The main mechanism of sintering is based on melting the eutectic Mg–Ca (a powder blend of Mg with Ca) or a mixture of pure Mg with the master alloy Mg–Ca. The melt covers the solid magnesium particles, reduces the oxide, and enhances sintering. This principle has been used to produce many biodegradable applications [15,16]. However, the use of Ca presents some challenges, such as high flammability. An alternative candidate to replace calcium could be zinc (Zn). The Mg–Zn system has limited solubility components in a solid state [17]. On the magnesium side, there is a solid solution with a maximum zinc solubility of 6.2% at 340 °C. Magnesium is practically insoluble in zinc, which stimulates intermetallic crystallization (MgZn , MgZn_2 , Mg_2Zn_3 , $\text{Mg}_2\text{Zn}_{11}$, and $\text{Mg}_{51}\text{Zn}_{20}$). Furthermore, Zn, like Ca, is a biological nutrient element, which is important for biodegradable alloys [18]. In vitro tests of Mg–Zn and Mg–Zn–Ca materials showed good cell adhesion and a controlled corrosion rate [19]. Zinc is widely used in manufacturing Mg–Zn alloys [20], but the nature of microstructure formation and sintering mechanisms remain poorly studied.

In this study, the Mg–(5, 10 wt. %) Zn alloys were prepared by pressing and sintering at a temperature of 430 °C with isothermal holding for 30 min in an argon medium. The contact angle on the Zn/MgO interface was determined, which is a fundamental parameter for reactions in solid–melt systems. The results of this study contribute to determining the driving forces of Mg activation in liquid phase sintering by Zn additions and provide the theoretical basis for optimizing the manufacturing of magnesium-based materials.

2. Materials and Methods

Mg (chips, 6–35 mesh, purity 99.98%, Sigma Aldrich, Saint Louis, MO, USA) and Zn (powder, 1–5 μm , purity 99.99%, Sigma Aldrich) were used as initial materials for the liquid phase sintering analysis (Figure 1). The Mg–5 wt. % Zn (Mg–5Zn) and Mg–10 wt. % Zn (Mg–10Zn) alloys were prepared by cavitation mixing in tetrahydrofuran liquid (Thermo Fisher, Waltham, MA, USA). A sonicator (UIP1000hdT, Berlin, Germany) was used to initiate the liquid vibrations. A portion of the powder was compacted by uniaxial pressing at 100–400 MPa using a steel die. Green samples were placed in a nickel crucible and sintered at 430 °C, with a holding time of 30 min in argon medium at a cooling rate of -5 °C/min . At 430 °C, the temperature was slowed down to prevent metastable phase crystallization. To compare the influence of zinc on the sintering process, a green sample of pure magnesium was sintered under the same conditions. The contact angle was measured using the sessile drop method [21]. During the procedure, high-purity argon was used to prevent Zn evaporation.

To measure the contact angle between Zn and MgO, the substrate was prepared by the oxidation of pure magnesium samples $30 \times 30 \times 12\text{ mm}$ at 550 °C for 8 h. A portion of zinc was placed on the substrate and melted at 440, 460, 480, and 500 °C for 20 min. The evolution of the contact angle was controlled using a camera and image acquisition/processing system.

The density of green and sintered materials was measured by the Archimedes method according to ASTM B962-23 [22]. Volume shrinkage was determined by changing the size of the samples. The phase analysis of the sintered materials was carried out using a Rigaku (Tokyo, Japan) Ultimate IV diffractometer (XRD) at a scan speed of $2^\circ/\text{min}$. True Sight X was used to analyze the chemical composition and distribution of elements. The compressive strength of sintered pure Mg and Mg–Zn alloys was studied using $\text{Ø}10 \times 10\text{ mm}$

cylindrical test specimens on a servo-motorized universal testing machine HD-B612-S (Haida International Equipment Co., Ltd., Dongguan, China) at a load rate of 2 mm/min.

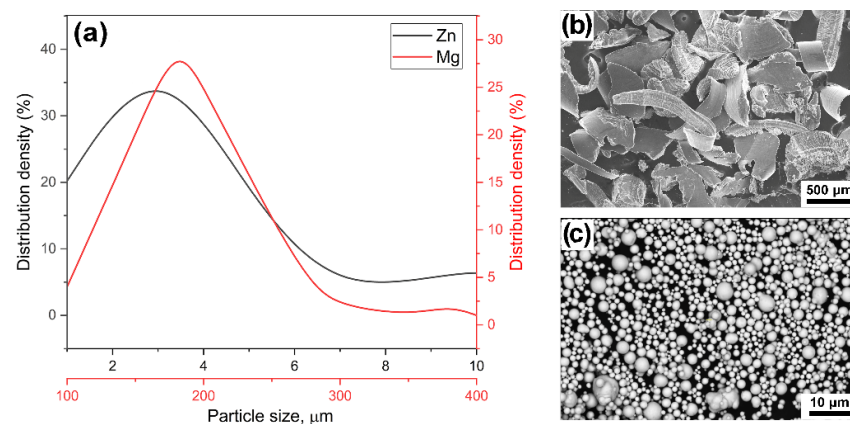


Figure 1. Characteristics of the initial materials. (a) Particle size distribution obtained via laser diffraction and (b) SEM morphology of magnesium and (c) zinc particles.

3. Results

3.1. Pressing and Sintering

Figure 2a,b show the influence of the zinc content on relative density and shrinkage. The Zn addition up to 10 wt. % reduces the relative density and limits the shrinkage of the powder body. At a zinc concentration of 5 wt. %, sintering occurs in a transient liquid phase (TLP) [23] within the α -Mg solid solution region [20]. The growth during the sintering of Mg–5Zn samples may have a diffusion nature. According to the works of I. Ya Frenkel [24,25], the sintering of multicomponent systems is significantly dependent on the ratio of interdiffusion coefficients. With a large difference in diffusion coefficients, porosity, and sample growth may occur. The growth of the samples, in this case, is due to the formation of a solid solution with a large specific volume [26]. Regarding the data on interdiffusion coefficients in the Mg–Zn system, it is known that the interdiffusion coefficient of zinc into magnesium is $2.67 \times 10^{-5} \text{ m}^2/\text{s}$ [27]. At the same time, it is not possible to find data on the diffusion of magnesium into zinc in literary sources. This is explained by the structure of the phase diagram, in which magnesium is practically insoluble in zinc.

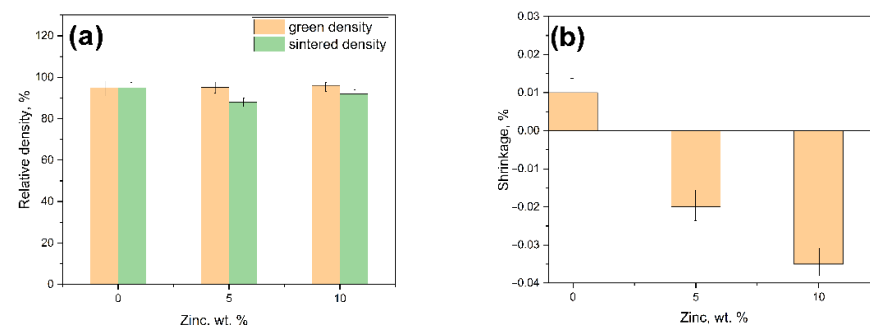


Figure 2. Relative density of green and sintered Mg and Mg–Zn alloys (a). Volume shrinkage of Mg and Mg–Zn alloys (b).

Das S. K. et al. [28] showed that the accumulation of magnesium atoms formed a new phase of the $\text{Mg}_2\text{Zn}_{11}$ intermetallic compound, the diffusion coefficient of which is $8.08 \times 10^{-14} \text{ m}^2/\text{s}$. The difference in diffusion coefficients can contribute to the manifestation of Frenkel effects [27] and, consequently, the growth of samples. Increasing the zinc concentration to 10 wt. % transfers the system to the region of hypoeutectic alloys and

accelerates the growth of samples. This can be associated both with the formation of a solid solution with a large volume and with the formation of an intermetallic MgZn [29].

3.2. Microstructural and Phase Analysis

Figure 3 shows the XRD patterns of the sintered pure Mg and Mg-5Zn, and Mg-10Zn alloys. The peaks of pure magnesium and the solid solution of zinc in magnesium are practically the same (Figure 3a–c). As can be seen in Figure 3b,c, all sintered Mg-Zn alloys exhibited an α -Mg, and intermetallics. $\text{Mg}_{51}\text{Zn}_{20}$ (formerly Mg_7Zn_3 [30]), and MgZn phases were found in Mg-Zn alloys. At a zinc concentration of 5 wt. %, the $\text{Mg}_{51}\text{Zn}_{20}$ phase is formed [31]. An increase in Zn content promotes the crystallization of MgZn and $\text{Mg}_{51}\text{Zn}_{20}$ intermetallics. The possible mechanism of MgZn can be the transformation of $\text{Mg}_{51}\text{Zn}_{20}$ into MgZn and α -Mg [32].

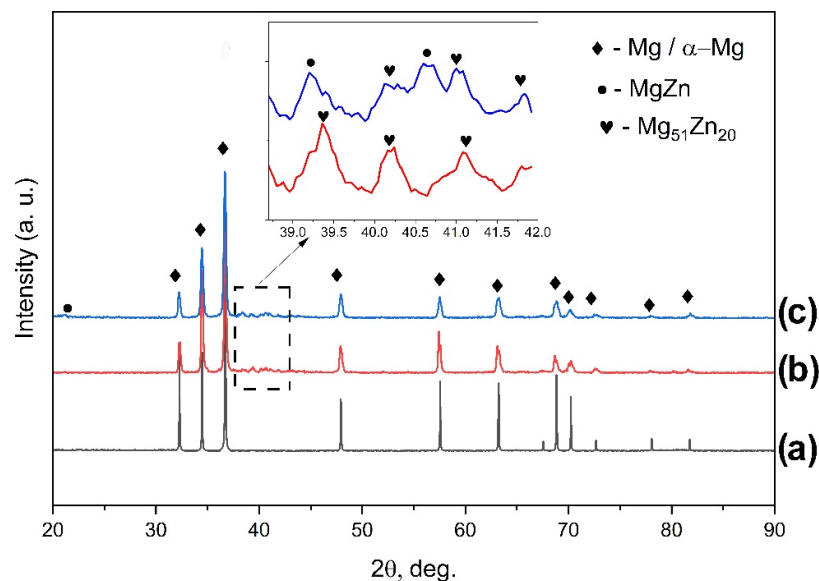


Figure 3. The XRD pattern of magnesium (a) and Mg-5Zn (b) and Mg-10Zn (c) alloys.

Figure 4a–f show the SEM images of magnesium alloys with different zinc contents. As can be seen from Figure 4a,b, pure magnesium forms the oxide layer on the surface, which inhibits the diffusion processes [33]. XRD (Figure 3a) and EDS point analysis (Figure 4b, Table 1) clearly show that the black layer around the particles corresponds with magnesium oxide. The addition of 5 wt. % Zn promotes the crystallization of the solid solution α -Mg and $\text{Mg}_{51}\text{Zn}_{20}$ (Figure 4c,d). According to the Mg-Zn binary phase diagram, the $\text{Mg}_{51}\text{Zn}_{20}$ intermetallic phase does not exist at 5 wt. % Zn [34]. This tendency for phase formation is characteristic of most magnesium, aluminum, and titanium alloys [35–40]. The presence of many intermetallics, which are easily formed and subsequently remain in the structure, is noted. In most cases, intermetallic compounds are very stable, and the diffusion of metal atoms from the matrix is inhibited [31]. Increasing the zinc concentration to 10 wt. % promotes the formation of a three-phase structure in the alloy (Figure 4e,f). MgZn and $\text{Mg}_{51}\text{Zn}_{20}$ were formed. The local transformation of the $\text{Mg}_{51}\text{Zn}_{20}$ phase into MgZn according to the eutectoid reaction is shown (Figure 4f). The partial transformation occurred due to the high cooling rate, which did not allow a full transition. The formation of a white coating on the furnace muffles was observed during the sintering of Mg-5Zn and Mg-10Zn alloys (Figure 4g). According to local EDS analysis, the particles corresponded to magnesium oxide (Figure 4h and Table 1).

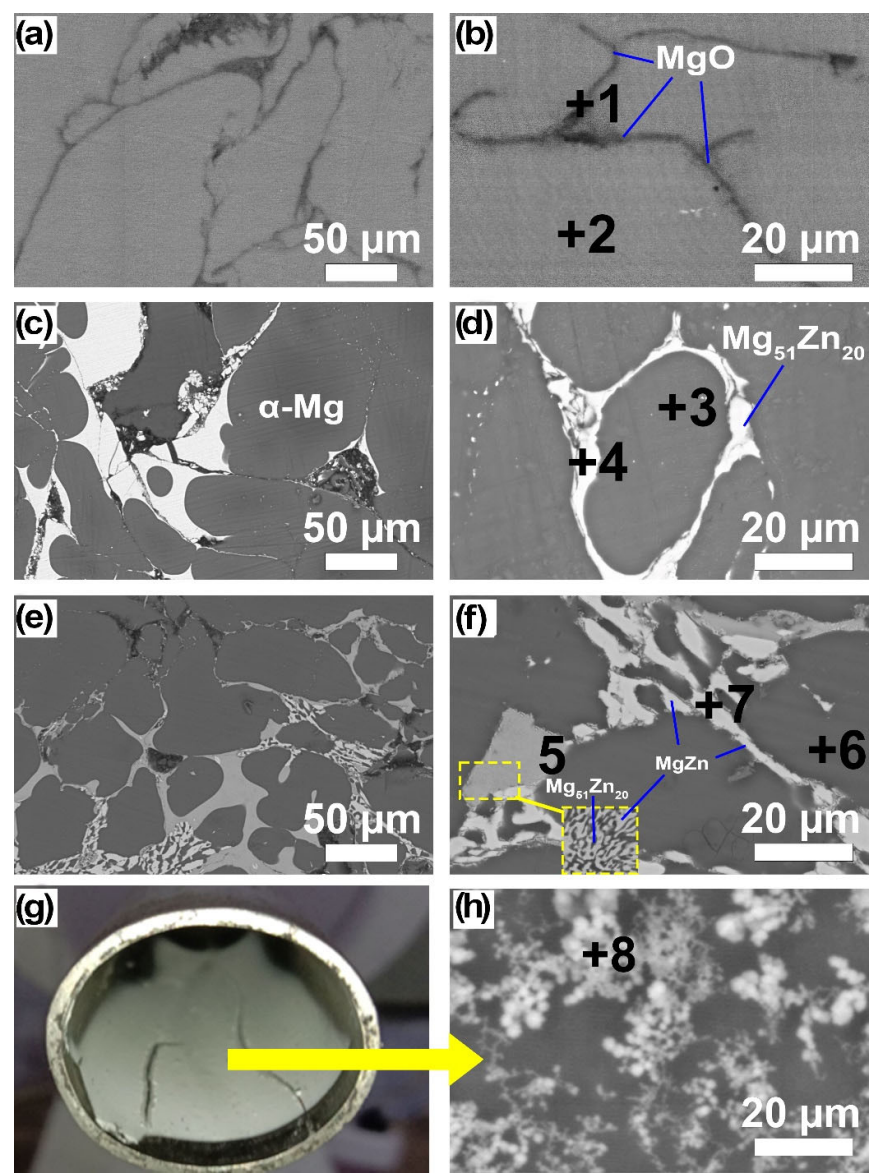


Figure 4. SEM image of sintered (a,b) pure Mg, (c,d) Mg–5Zn, (e,f) Mg–10Zn, and (g,h) white coating on cold side muffle. The numbers in the image refer to the EDS analysis results, which are showcased in Table 1.

Table 1. EDS results from the areas marked in Figure 4.

Point	Elements, wt. %		
	Mg	Zn	O
1, 8	50.8	-	49.2
2	99.17	-	0.83
3	91.8	7.2	1.0
4	47.4	49.4	3.2
5	48.8	48.8	2.4
6	89.8	7.6	2.3
7	20.7	75.6	3.7

The structure of the alloy is similar to most known magnesium-based materials, with the formation of a solid solution and intermetallic compounds. It is important to note that the presence of magnesium oxides on the surface does not prevent the formation of alloy structures. The microstructure of the alloy highlights the activating properties of zinc

during sintering and its interaction with magnesium oxides. The EDS analysis of the areas of Mg, Mg–5 Zn, and Mg–10 Zn shows a decrease in oxygen content from 9.8 wt. % to 3.1 wt. %. This effect requires a more detailed analysis of the processes at the Mg/Zn/MgO phase boundaries.

3.3. Compressive Strength of Mg–Zn Alloys

Figure 5 shows the compressive strength of sintered pure Mg and Mg–Zn alloys. Pure magnesium, due to oxidation at the grain boundaries, lacks sufficient chemical contact between the particles. Therefore, sintered Mg has a compressive strength of 92–95 MPa. The compressive test indicated that an increase in zinc content also increased the compressive strength to 250 MPa. The increase in compressive strength could also be due to grain boundary purification and crystallized intermetallics. In general, intermetallic compounds have a high hardness and Young’s modulus, which promote the higher mechanical properties of alloys. However, the content of zinc must be precision-controlled. According to Yunpeng Hu et al. [20], an increase in zinc content up to 30 wt. % promotes the degradation of mechanical properties. The crystallization of a large amount of brittle intermetallics is the main reason for this loss of mechanical strength. A comparison of the experimental compressive strength with commercially available magnesium alloys is given in Table 2.

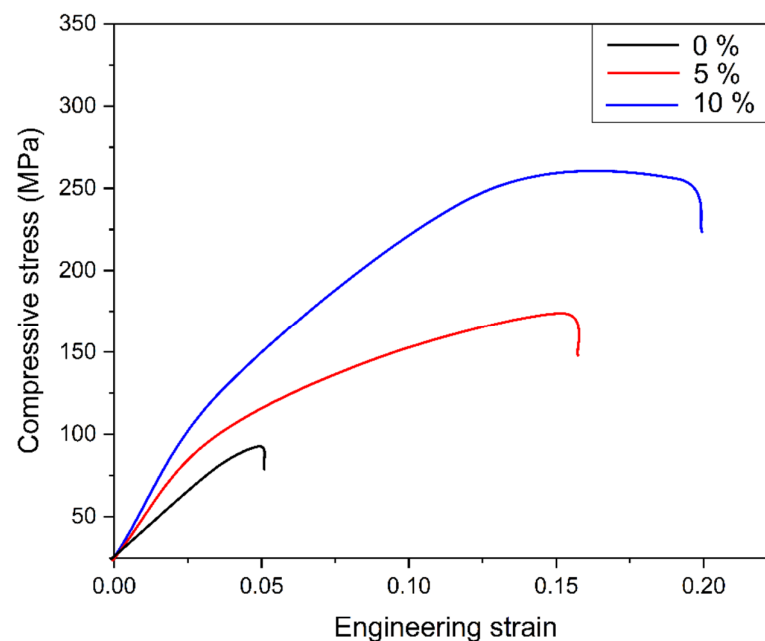


Figure 5. Compressive strength of Mg and Mg–Zn alloys.

Table 2. Compressive strength of commercially available magnesium alloys.

Composition	Compressive Strength, MPa	Ref.
Mg–10Zn	210	[20]
Mg–5Ca	250	[41]
WE43	430	[42]
ZK61	250	[43]
Mg–Zn–Ca–Y	100–170	[44]
Mg–5Zn	170	This work
Mg–10Zn	260	

3.4. Interaction at Mg/MgO/Zn Interfaces

One of the most important parameters in systems with a liquid phase is the presence of wettability. To understand the influence of zinc on the sintering process, contact angle measurements between Zn and MgO were carried out using the sessile drop method. It

is known that MgO has a porous structure, so the substrate was not made to be dense to replicate real interaction conditions as closely as possible. From a thermodynamic point of view, the zinc melt does not reduce MgO ($\Delta G = 250$ kJ/mol). However, a possible mechanism involves Zn penetration between the MgO particles and the destruction of the oxide layer. As shown in work [45], this can occur in MgO–Ti, MgO–Cr, and MgO–Pb systems, where the melt penetrates between the grains of MgO or dissolves it. Figure 6a shows the general view of the MgO/Mg substrate. The SEM image (Figure 6b,c) and elemental mapping analysis of the magnesium oxide layer indicate a low-density structure with weak adhesion to the base's body. The contact zone between zinc and MgO shows (Figure 6e, yellow arrow) that closed porosity and low wettability can prevent zinc melt penetration inside the porous MgO skeleton.

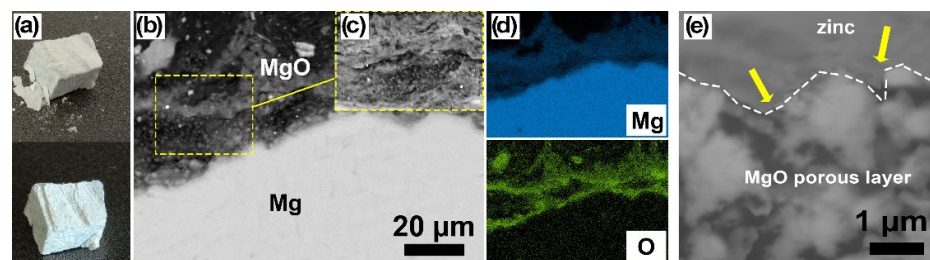


Figure 6. General view (a) and microstructure of the substrate Mg/MgO (b,c); EDS elemental mapping for Mg/MgO layer (d). Contact zone between Zn melt and porous MgO layer. Yellow arrows indicate the penetration of zinc melt into porous MgO (e).

Figure 7 shows the evolution of the contact angle between Zn and MgO at 440, 460, 480, and 500 °C. An increase in temperature reduces the contact angle [42]. The minimum contact angle is 60° at 500 °C, but it is insufficient for successful liquid-phase sintering [32,46]. This also indicates the absence of interactions between the substrate and the melt. The change in the contact angle contradicts the experimental results on sintering. It is speculated that the penetration of zinc is significantly influenced by the thickness of the oxide layer. Therefore, an analysis of structure formation was carried out during the primary oxidation of magnesium shavings for 3 h at 450 °C. The shavings were rolled into a zinc cartridge (Figure 8a) and heated to 430 °C, holding for 5 min.

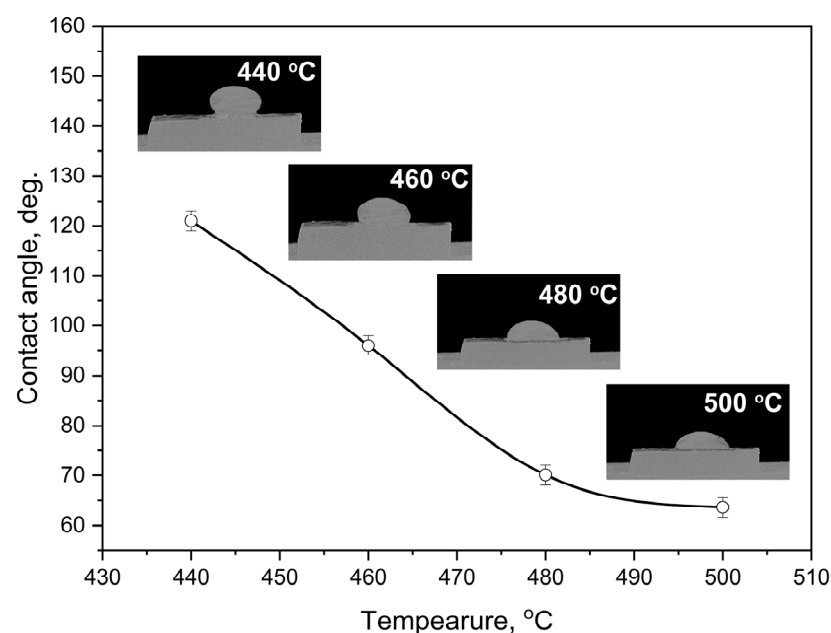


Figure 7. Evolution of the contact angle on the MgO/Zn interface at different temperatures.

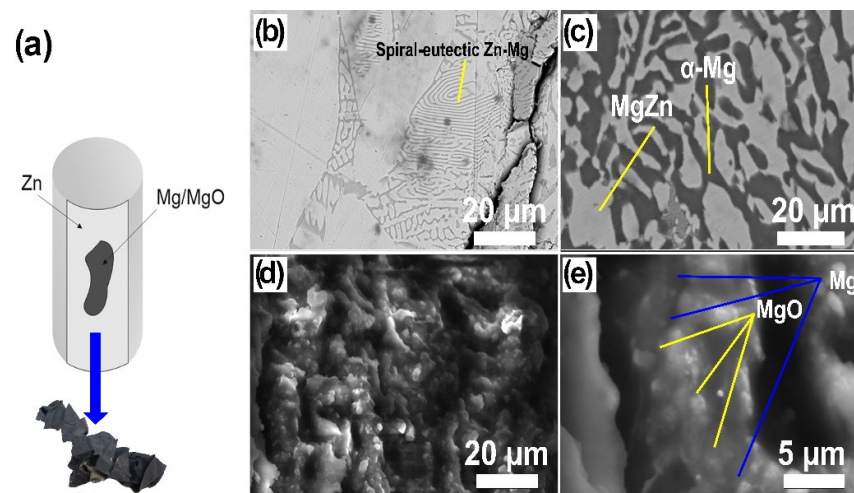


Figure 8. (a) Zinc sleeve with Mg/MgO; (b) microstructure on the zinc side. (c) Microstructure on the magnesium side. (d,e) Morphology of oxide layers on the surface of magnesium.

On the zinc side, the formation of Zn–Mg spiral electroeutectic was identified (Figure 8b). Eutectic Zn–MgZn₂ is a two-layer package twisted into hexagonal rolls and conically expanded on both sides of the base of the MgZn₂ crystal. The growth of the eutectic is based on the formation of a colony based on the main MgZn₂ phase, forming a funnel in the plane. The increased concentration of zinc inside promotes the formation of the nuclei of another phase that grows along the surface of the funnel. Compatible growth along the funnel walls promotes the filling of spiral rolls with two eutectic phases [47]. On the magnesium side (Figure 8c), a two-phase microstructure was identified based on α-Mg and MgZn. The structure of magnesium (Figure 8d,e) after oxidation consists of locally non-uniform MgO particles and free surfaces. Due to the lack of a dense structure in the oxide layers and their uneven distribution over the surface of the particles, zinc can penetrate magnesium grains with the formation of a solid solution and intermetallics.

The crystallization of new phases also contributes to a change in crystallographic planes and a decrease in coherence between the oxide layers [47,48] and the alloy, which can destroy and remove MgO from the surface. Removing magnesium oxide from the surface allows conditions to be created for diffusion processes between zinc and magnesium atoms with the formation of intermediate phases.

4. Discussions

The generalized sintering mechanism is shown in Figure 9. At the initial stage of interaction, with a thin layer of oxide on the surface of magnesium particles, the zinc melt penetrates through the free pore spaces to the free surface and reacts with it (Figure 9a). In the contact zone, the magnesium surface is saturated primarily with zinc (Figure 9b). The detachment of MgO particles occurs because of a change in the crystallographic planes involving non-wettable MgO by molten zinc, and there is also a significant density between MgO/Zn, which contributes to the rise in slag in the form of oxides to the surface of the melt.

Under normal conditions, zinc can evaporate during melting due to low vapor pressure [49], but intense gasification occurs at its boiling point (906 °C). Exothermic reactions [50] between zinc and magnesium are possible; locally, they can raise the temperature to a boil. During the melting of Zn in the green body, magnesium oxide detaches from the base particle; since MgO is poorly wetted by zinc, the oxide particles migrate to the surface along porous capillaries. Accordingly, zinc atoms, which vaporize from the surface, can capture part of the magnesium oxide and precipitate in places of condensation. This was confirmed by the presence of a white coating in the areas of the cold ends of the muffle (Figure 4g,h). As area EDS analysis showed, the addition of zinc reduces the oxygen content

from 9.8 % (for pure magnesium) to 3.1% (for the Mg–10Zn alloy), which indicates the partial removal of MgO. The further saturation of the surface with zinc leads to the local formation of MgZn/Mg₅₁Zn₂₀ intermetallics. With a thick oxide layer on the surface of about 30 µm, the reaction between zinc and magnesium does not occur because a closed system of pores and channels and the low wettability of MgO by Zn do not allow the melt to encounter the pure Mg surface (Figure 6e). At this stage, the contact angle plays a significant role, which is at the level of 50 °C.

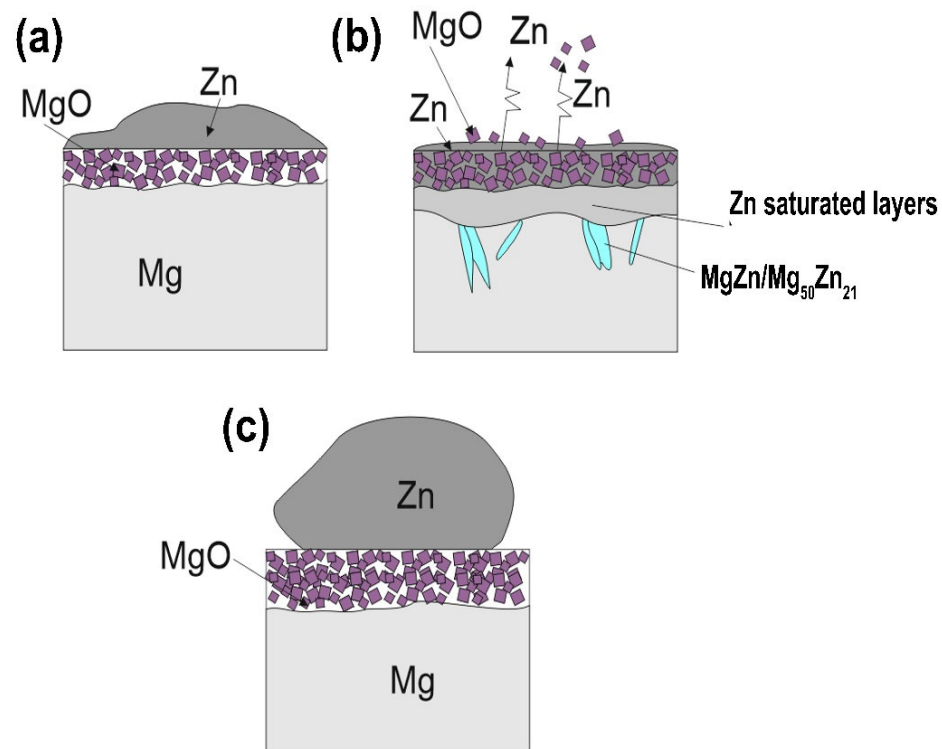


Figure 9. Activation mechanism of magnesium sintering with zinc additives. (a) First stage of the migration of zinc through MgO to the magnesium surface; (b) second stage of sintering the reaction between the melt and magnesium surface; and (c) the influence of oxide layer on zinc penetration.

Some features in the sintering mechanism can be realized for Mg–10Zn alloys. At 10 wt. % Zn, sintering occurs in the region of hypoeutectic alloys [20]. After the primary melting of zinc and the removal of MgO from the surface, during the reaction of Zn and Mg, the sintering temperature can decrease due to the formation of eutectic (at the eutectic point 347 °C [17]). The combination of zinc’s action on the magnesium surface, the liquid phase sintering, and eutectic melting promotes the activation of the sintering process. Obtaining eutectic is typical for many magnesium alloys with Zn, Ca, Y, and Nd [13,49,50], which significantly reduces the negative impact of oxides on the sintering process.

5. Conclusions

The influence of zinc additions on magnesium powder was studied. The experimental results reveal the following.

- (1) The relative density of Mg and Mg–5, 10 wt. % Zn alloys after sintering in an argon environment at 430 °C and holding for 30 min are 95%, 88% and 92%, respectively. Growth during the sintering of Mg–5Zn and Mg–10Zn is due to the crystallization of phases with larger volumes and the action of the Frenkel effect.
- (2) In the structure of pure magnesium, an oxide was found, which accumulated at the boundaries between the particles, resisting sintering. Zinc additives from 5 to 10 wt. % contributed to the formation of α -Mg, MgZn, and Mg₅₁Zn₂₀.

- (3) The contact angle between the zinc melt and the MgO substrate was 120° at 440 °C and decreased to 65° at 500 °C. The reactions between the melt and the substrate were not identified.
- (4) The mechanism of magnesium sintering with zinc addition is shown. The mechanism is based on the following stages: the penetration of zinc to oxide-free surfaces; reactions to form a solid solution, intermetallics; the removal of magnesium oxide from the particle surface due to a change in the crystallographic orientation of the base phase and low wettability of the zinc melt; oxide particles were deposited on the surface of the sample in the form of slag.

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