Study on the Mg-Zn binary alloys fabricated by gas-phase alloying

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Abstract. By adjusting the evaporation temperatures and changing the Mg/Zn atomic ratios (in the range of 0.5 to 4), various Mg-Zn binary alloys were fabricated using a novel technique named as gas-phase alloying. The theoretical calculation by the formula of saturated vapor pressure is to determine the evaporation temperature, which is 900-1200K for Mg and 700-1000K for Zn. The specimens were subjected to SEM, EDS, and Brinell hardness examinations. The results obtained show that, regardless of atomic ratios, microstructures include Mg$_2$Zn$_3$ particles and α-Mg matrix, the former is uniformly distributed into the latter. However, with increasing Mg/Zn atomic ratios, the microstructural transformation occurs from columnar precipitation to granular one.

1. Introduction
With the significant advantages of low density, high specific strength, Mg-based alloys are desirable materials for the transport industry and replace the aluminum-based alloys in some particular cases [1-2]. It is well known that zinc is a preferable alloying element and can form the different intermetallic phases, especially Mg$_2$Zn$_3$ [3-4]. However, Mg/Zn atomic ratio can dramatically change the microstructure and influence the properties of Mg-Zn alloy.

Because vapor condensation is the effective and simple technology for fabricating new materials or coatings, Xi et al. [5] prepared the Zn-Mg alloy through the chemical vapor deposition (CVD) method and observed the self-corrosion current density and impedance resistance of the alloy. In the paper, the authors aimed to produce Mg-Zn alloys with indirectly adjustable Mg/Zn ratios under the vacuum conditions and to investigate the effect of Zn content on the microstructure and formation of Mg$_2$Zn$_3$ intermetallic particles. Besides, the expected findings will be used to substantiate the idea of fabricating a novel composite reinforced by intermetallic Mg$_2$Zn$_3$ particles.

2. Experimental processing
The Mg-Zn binary alloys were fabricated by the evaporation-mixture-condensation method (nominated as gas-phase alloying technique). Figure 1 shows a conceptual diagram of the experimental device. The crude Mg (99.96wt.% purity) was evaporated in chamber 1, and the crude Zn (99.98wt.% purity) was evaporated in chamber 2. Two kinds of metal vapors entered into chamber 3 (700±10K), simultaneously, and were mixed under the function of the baffles inside chamber 3. Subsequently, the mixture of metal vapors was condensed inside chamber 4 (600±10K). The whole device was made up of stainless steel. There are two similar graphite crucibles fixed inside chambers 1 and 2, respectively, the crude Mg and Zn (similar in size and shape) were loaded into the graphite crucibles. During every experiment, the system vacuum degree was 30±5Pa and the soaking time was 0.5h at a certain
temperature. Microstructure and elemental analysis were conducted by using a TESCAN VEGA 3 scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS).

![Conceptual diagram of the gas-phase alloying device.](image)

**Figure 1.** Conceptual diagram of the gas-phase alloying device.

To ensure the formation of uniform Mg/Zn binary alloys, the preferable mixture degree of two metal vapors is very critical; therefore, several baffles were set up in chamber 3. These baffles not only are beneficial to improve the mixture degree but also can reduce the kinetic energies of two metal vapor atoms and favor the condensation [6]. However, the more baffles cannot ensure the mixture vapors to successfully condensate inside chamber 4 successfully. According to the preliminary experiments, the appropriate number of baffles is four-layer.

3. **Theoretical analysis and calculation**

3.1. **Determination of the ratios of Mg/Zn**

In the study, the Mg/Zn atomic ratio is the most important factor to control the microstructural characteristic and related to the evaporation rate. According to the literature [6-7], the vapor rate of certain metal can be calculated by formula (1), and the saturated vapor pressure of Mg and Zn metals at certain temperature can be computed through equations (2) and (3), respectively, and the calculated results were listed in table 1.

\[
\begin{align*}
  w_i &= 1.574\alpha P \left( \frac{M}{2\pi R T} \right)^{1/2} \\
  \lg P^*_{Mg} &= \frac{7550}{T} - 1.41 \lg T + 14.90 \\
  \lg P^*_{Zn} &= \frac{6620}{T} - 1.255 \lg T + 14.465
\end{align*}
\]

where \( w_i \) is evaporation rate for certain metal, \( \alpha \) is the condensation constant for most crystalline metals approaches unity, \( M \) is the molar mass of metal (g/mol), \( P^*_i \) is the saturated vapor pressure (Pa), \( T \) is the temperature in Kelvin scale (K).
Table 1. The saturated vapor pressures of Mg and Zn at different temperatures.

| T(K) | 700  | 800  | 900  | 1000 | 1100 | 1200 |
|------|------|------|------|------|------|------|
| $P'_{\text{Mg}}$ | -    | -    | 220.08 | 1309 | 5557.8 | 18348 |
| $P'_{\text{Zn}}$ | 27.384 | 352  | 2522.3 | 120226 | -    | -    |

Then, the vapor ratio for Mg/Zn can be determined using the following equation (4).

$$\frac{w_{T_{\text{Mg}}}^n}{w_{T_{\text{Zn}}}^m} = \frac{P_{M_{\text{Zn}}}}{P_{Z_{\text{Mg}}}} \left(\frac{M_{\text{Mg}}}{M_{\text{Zn}}}\right)^{\frac{1}{2}}$$

Therefore, $w_{M_{\text{Mg}}}^{1200} / w_{Z_{\text{Mg}}}^{1000} = 0.4695$, $w_{M_{\text{Mg}}}^{1100} / w_{Z_{\text{Mg}}}^{900} = 0.94438$, $w_{M_{\text{Mg}}}^{1000} / w_{Z_{\text{Mg}}}^{800} = 2.021$.

where superscript and subscript in $w_i^T$ indicate the evaporation temperature and certain metal, respectively. To simple observation, the ratios of Mg/Zn for various specimens are approximate to 0.5, 1.0, 2.0 and 4.0, the corresponding evaporation temperatures for the chamber 1 and 2 are shown in table 2.

Table 2. The different evaporation temperatures for various specimens.

| Vapor ratio for Mg/Zn (at.%) | 0.5  | 1   | 2   | 4   |
|-----------------------------|------|-----|-----|-----|
| Mg evaporation temperature (K) | 900  | 1000 | 1100 | 1200 |
| Zn evaporation temperature (K) | 700  | 800  | 900  | 1000 |

4. Formation mechanism

When two kinds of the vapors were mixed in chamber 3, which temperature is lower than the dew point of Mg vapor and higher than the dew point of Zn vapor [7], Mg vapor will transform into Mg tiny droplets following equation (5), and Zn vapor cannot be converted into droplets and still keep as a state of steam flow under the vacuum function.

$$M_{\text{Mg}}(g) = M_{\text{Mg}}(1)$$

Some tiny Mg droplets can collide with the Zn vapor atoms, some reactions between them will take place via equation (6), and the intermetallic compound Mg$_x$Zn$_y$ will be formed, these particles are expected to act as the reinforcement of novel composite [8].
\[ x\text{Mg}_g + y\text{Zn}_g = \text{Mg}_x\text{Zn}_y \quad (6) \]

But a large portion of tiny Mg droplets cannot collide with the Zn vapor atoms which directly reach condensing wall and rapidly solidify at orientated growth. This part of condensation production has less Zn content and can be expected to act as the matrix of novel composites reinforced by the intermetallic compound.

5. Results and Discussion

Figure 2 gives the microstructures of alloy under the different atomic ratios of Mg/Zn. When the atomic ratio is 0.5, namely, the Zn vapor content is much higher than that of the Mg content. The microstructure is comprised of sizeable white flake precipitation and granular production, the size of them is less than 5 micrometer in width, as seen in figure 2(a). Based on the EDS results, Mg content in the black area (point A in figure 2(a) and table 3) is rich, and Zn content in the white area (point B in figure 2(a) and table 3) is rich. The white phase is determined by Mg\text{7Zn}_3, and the black area belongs to the \alpha-Mg matrix, in which the Zn content is less. This indicates that some Mg droplets collided with Zn vapor, the peritectic reaction can be carried out, and the reactive products Mg\text{7Zn}_3 can directly grow perpendicular to the cooling surface. At the same time, non-collided Mg droplets were directly cooled as the matrix. These findings are agreeable to the front mechanism interpretation.

![Figure 2](image_url)

**Figure 2.** Microstructures of Mg-Zn alloys with different vapor ratios: (a) 0.5, (b) 1, (c) 2, (d) 4.
When the atomic ratio of Mg/Zn is added up to 1, the greater flake precipitation can be avoided, the more obvious orientated growth and the column distribution can be found, as well as some finer granular precipitation can be detected between column structure. According to the EDS results (point C in figure 2(b) and table 3), the finer particles are deemed to Mg:Zn₁ and not other intermetallics, such as MgZn₂, MgZn, etc. These phenomena adequately indicate that the trend for the formation of Mg:Zn₁ is superior to other intermetallic compounds.

When the atomic ratio of Mg/Zn is up to 2, the white and black structure is still the main characteristic as shown in figure.2(c). Due to the solidification of a larger of Mg droplets, releasing latent heat can melt a part of the inter-metallic compound and leads to the occurrence of rounded shape production (point E in figure 2(c) and table 3). Meanwhile, Zn atoms from the dissolution of Mg₂Zn₁ diffuse into the black area and increase Zn content in the dark area (point D in figure 2(c) and table 3).

When the maximization of the atomic ratio is 4, the quantity of Zn vapor is too less to ensure the formation of the continuous columnar production, instead of the granular precipitation. From the Figure 2(d), it can be seen that the initial reactive product present very fine particles which will grow gradually and may provide a more substantial granulate precipitation. These particles are expected to improve the properties of Mg-based composite (point F in Figure. 2(d) and Table 3).

From above analysis, it is concluded that, regardless of the Mg/Zn ratios (in the range of 0.5 to 4), the Mg:Zn₁ is the only kind of intermetallic compound, and presents a change from a columnar structure to a granular one with increasing the Mg/Zn atomic ratios.

Since the size of intermetallic particles is very small, the pressure head of microhardness is not able to sufficiently load on the particle. Therefore, Brinell hardness is selected to compare the difference in term of hardness. Figure 3 gives the decreasing trend of hardness with increasing the Mg/Zn atomic ratios, the maximum value (127.2±0.5HB for the ratio of 0.5) is nearly 1.5 times higher than the minimum value (82.3±0.5HB for the ratio of 4), which exceeds the hardness of AZ31 in a forging state [9]. It can be interpreted by the fact that abundant Zn vapor can react with the Mg droplets and contributes to the formation of plenty of Mg:Zn₁ compounds which has higher hardness and expected to act as the reinforcement of composite.

| Table 3. EDS for different points in figure 2. |
|---|---|---|---|---|---|---|---|
| Point | A | B | C | D | E | F | G |
| Mg(at.%) | 71.41 | 95.02 | 68.30 | 94.14 | 73.52 | 75.75 | 92.02 |
| Zn(at.%) | 28.59 | 4.98 | 31.70 | 5.86 | 26.48 | 24.25 | 7.98 |
Figure 3. Hardness variation with the Mg/Zn ratios.

6. Conclusions
Mg-Zn binary alloys were prepared by gas-phase alloying technique under the vacuum condition. The ratios of Mg/Zn vapor atoms can be explained and effectively controlled through the difference of evaporation temperatures. When the ratio of Mg/Zn is higher, it is advantageous to form Mg$_7$Zn$_3$ particles. When the ratio of Mg/Zn is lower, Mg$_7$Zn$_3$ particles present oriented growth and columnar structure. Regardless of the Mg/Zn ratio, all condensations have high hardness. These findings substantiate the idea to fabricate a novel composite reinforced by intermetallic Mg$_7$Zn$_3$ particles.

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