Effect of heat treatment on the electrical conductivity of ZM51 magnesium alloy

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Abstract. The microstructures and electrical conductivity of extruded Mg-5.38 wt.%Zn-0.88 wt.%Mn (ZM51) magnesium alloys under four different heat treatments (T5: single aging, two-stage aging; T6: T4+single aging, T4+two-stage aging) were investigated by optical microscopy (OM), X-ray diffraction (XRD), transmission electron microscopy (TEM) and conductivity test. The results show that the electrical conductivity of alloys after different heat treatments was increased with the aging time increasing identically. The conductivity of T6 ZM51 alloy is lower than that of T5 treatment alloy, and the conductivity of alloy with two-stage aging is higher than that of alloys with single-stage aging. In the two-stage aging, the time of pre-aging at low temperature formed dense GP zones which can serve as the nucleation core of the \( \beta_1' \) phases, and the formed \( \beta_1' \) phases are more diffuse and fine, and the scattering of free electrons are lower. The electrical conductivity of the alloy increased first and then reduced with the increase of the pre-aging time, and the reason is that the alloys form a more diffuse GP zones after pre-aging for 32h, which can be used as the heterogeneous nucleation core of \( \beta_1' \) phases, so that the precipitation of the \( \beta_1' \) phases are more finely dispersed, thereby increasing the scattering capacity of free electrons.

1. Introduction

Magnesium alloys, as the lightest metal-based structural materials, have attracted much attention of researchers because of their high specific strength, excellent damping property, good electromagnetic shielding, and they are environmentally friendly [1-3]. Mg–Zn-based alloy is one of the earliest developed precipitation-hardening magnesium alloys. The equilibrium solid solubility of zinc in magnesium decreases mainly with the decrease of temperature, and controlled decomposition of supersaturated solid solution of zinc in magnesium can produce significant age-hardening effect. Relevant research shows that due to the precipitation of the transition phase \( \beta_1' \), Mg-Zn alloys have a large aging hardening response, so it has good strength and ductility [4,5]. Therefore, Mg–Zn alloys are suitable for developing high strength wrought Mg alloy. According to relevant research, the addition of Mn element in Mg-Zn alloys can refine the grain size, improve casting performance and forming performance of the extrusion process. The alloy has excellent industrial properties such as low cost (without Zr and rare-earth elements), high strength and low extrusion temperature, which provides meaningful opportunities for lightweight applications in automotive, aerospace, and 3C (computer, communication and consumer goods) industries.
At present, there are many studies on Mg-Zn-Mn alloy, focusing on the evolution of microstructure during the heat treatment, improving the strength and thermal conductivity of alloy by adding trace alloy elements, deformation and heat treatment. It is reported that the aging sequence of Mg-Zn system alloy is as follows: SSSS→GP zone→β′→β′→β [6].

Studies have shown that the GP zones precipitate only in the low temperature range (<110℃), and the metastable phases precipitate directly from the matrix without the presence of GP zones when the temperature is higher than 110℃ [7]. Besides, many researches show that the rod-like β′ phases which are metastable transition phases and cohere with the Mg matrix are main strengthening phases. While the metastable transition phases plate-like β′ semi-cohere with the matrix and the aging strengthening effect is poor. Therefore, the researchers explored the heat treatment system, in order to improve the precipitation quantity and density of β′ phases, so as to improve the strength of the alloy. Oh-Ishi et al. [8], Park et al.[9], and Buha [10] successfully formed GP zones in the Mg-Zn-based alloys by using the method of pre-aging. They reported that GP zones could be used as the heterogeneous nucleation center when the metastable phases precipitate at high temperature, thereby they could increase the density of precipitates and improve the alloys aging strengthening effect. Zhang [11] and Yuan [12] performed the solution treatment on the Mg-Zn-Mn alloys before aging to improve the dynamic precipitation of solute atoms, and the strengthening effect of alloys is better than that of T5 treatment.

However, there are few studies about the effect of different heat treatment conditions on the electrical conductivity and thermal conductivity of Mg-Zn-Mn alloy. Most of the studies on the Mg-Zn-Mn alloy tend to focus only on the effect of the precipitates on mechanical properties during the aging process.

In the present work, the effect of different heat treatments on the electrical conductivity of as-extruded Mg-Zn-Mn alloy was systematically analyzed by measuring the conductivity of Mg-Zn-Mn alloy in different heat treatment systems and combining with microstructure evolution.

2. Experimental

The material used in the present study with a nominal composition of Mg-5.38 wt.%Zn-0.88 wt.% Mn, referred to as ZM51 here onward. Commercial high-purity Mg, Zn and master alloys Mg-3wt%Mn were used to prepare the cast alloy, and the size of the ingot was Φ650mm×500mm. The experimental ingots were homogenized at 370 ℃ for 24 hours, and then hot extruded at 350℃ with a reduction ratio of 7, and the section size of the bar is 450mm×100mm.

Four heat treatment systems are adopted in this paper: T5: Single aging, two-stage aging. T6: solution-treated (T4) followed by single aging and solution-treated (T4) followed by two-stage aging treatment (The selection of the temperature peak aging treatment is based on the previous work). All the samples were followed by water quenching. The specific treatments are shown in Table 1.

The microstructure of as-solution alloy was studied by optical microscopy (OM). The constituent phases of the solid solution and as-pre-aging alloys were identified by X-ray diffraction of Cu Kα radiation. The electrical conductivity for the aging samples were measured by an eddy-current device at 25℃. The Vickers hardness measurement after aging was performed at 29.42N load.

| Table 1. Heat treatment parameters of the ZM51 alloys. |
|------------------------------------------------------|
| Heat treatment   | Parameter            | Solution Temperature (℃) | Time (h) | Pre-aging Temperature (℃) | Time (h) | Aging Temperature (℃) | Time (h) |
|------------------|----------------------|--------------------------|----------|--------------------------|----------|-----------------------|----------|
| Single aging     |                      |                          |          |                          |          | 175                   | 0~24     |
| Solution + Single aging |                  | 400                      | 1.5      |                          |          | 175                   | 0~24     |
| Two-stage aging  |                      |                          |          |                          |          | 90                    | 8~32     | 175                   | 0~24     |
| Solution + two-stage aging |                | 400                      | 1.5      | 90                       | 8~32     | 175                   | 0~24     |

3. Results and discussion

3.1. The microstructure of ZM51 alloy
Figure 1 shows optical micrographs of the extruded and solution (T4) alloy. In the extruded alloy, there is an obvious extrusion streamline formed by crushing the second phase particles which are not dissolved by homogenization treatment. And it can be seen that there are no obvious compounds in addition to the \(\alpha\)-Mn phases precipitated during solution treatment in the matrix of the tested alloys. TEM was used to observe the ZM51 magnesium alloy as extruded, pre-aging at low temperature for 32h and after solution at low temperature for 32h. The results are shown in figure 2. As shown in the figure, there are high density dislocations in the as extruded alloy, and there are still high density dislocations in the alloy after direct pre-aging for 32h. It can be seen from figure 2(c) and 2(d) that a more diffuse GP zones with a size between 2 and 5 nm was formed after 32h of pre-aging at 90°C. However, compared with the direct low-temperature pre-aging for 32h, the GP zones of the alloy after solution treatment for 32h was more and more dispersed. No obvious precipitates are formed at the same time. The XRD phase determination of the alloys in the state of solution and pre-aging 32h after solid solution are shown in figure 3. It can be seen that after the T4 treatment, there are no obvious diffraction peak of the second phase from the pattern except for the \(\alpha\)-Mg phases and the \(\alpha\)-Mn phases, Hence, it could be considered that the second phase basically remelted. Moreover, the results show that there is no significant increase in the second phase diffraction peak in the XRD pattern for the as-pre-aging alloys.

![Figure 1. Optical micrographs of ZM51 alloys: (a) as-extruded; (b) after solution treatment](image)

3.2. The hardness of ZM51 alloy

Figure 4 shows the effect of different heat treatments on the hardness of ZM51 magnesium alloys. According to the picture, the hardness of the alloy after different heat treatment increased rapidly at first followed by a wave-like slow rise. As shown in figure 4(a), the hardness of the alloy treated with T4+single aging is lower than that of single aging before aging for 10h. After 10h, the hardness of T4+single aging treated alloy is greater than that of single aging. In figure 4(b), the hardness of the two-stage aging alloy is greater than the single aging during the aging time, and the value of the alloy reaches the hardness peak which is 73.8HV after aging for 10h treated by the two-stage aging, and the peak aging time was significantly reduced. Comparison of hardness of alloys between T4+single aging treatment and T4+two-stage aging treatment is displayed in figure 4(c). We can see that the alloy treated with T4+two-stage aging reached the peak value of hardness earlier than that of T4+single aging. And the peak hardness of T4+two-stage aging treatment is 75.2HV, which is significantly higher than that of the alloy treated with T4+single aging.
Figure 2. HRTEM images of ZM51 alloys: (a) as-extruded; (b) and (c) direct pre-aging’ for 32h; (d) solution treatment+ pre-aging for 32h.

Figure 3. X-ray diffraction patterns of ZM51 alloys under different heat treatments.

The hardness of ZM51 magnesium alloy is up to the size, morphology, quantity and distribution of the second phase in the aging process. After solution treatment, the solute atoms are dissolved back, and the degree of lattice distortion increases. However, the solid solution treatment will lead to the reduction of the second phase in the alloy, which will lead to the reduction of the hardness. At the same time, the supersaturation of solute atoms in matrix is increased after the solution treatment, and the precipitation power increases, leading to rapid precipitation of the second phases during the aging process. Therefore, compared with T5 treatment, the hardness of alloys with T6 treatment increased faster, and reached the peak value of hardness earlier.

GP zones can be used as effective nuclei for $\beta_i^{'}$ phases for the next step aging at a higher temperature, and the $\beta_i^{'}$ phases are much fine and more dispersed after the later step aging. These precipitates, which are coherent with the matrix and have small spacing, can strongly block the movement of dislocations.
Therefore, compared with single aging, the hardness of alloys with two-stage aging treatment increased faster, and reached the peak value of hardness earlier.

Figure 4. Age-hardening curves of ZM51 alloys after different heat treatments.

3.3. The effect of heat treatments on the electrical conductivity of ZM51 alloy

Figure 5 shows the influence of different heat treatments on the electrical conductivity of ZM51 magnesium alloy. It is observed that the electrical conductivity after different heat treatments increased with the aging time increasing, and it increased rapidly at the early stage, then rising slowly. As shown in figure 5(a), the conductivity reduced from 16.1 MS/m to 15.7 MS/m after solution treatment. Besides, the conductivity of the alloy treated by T6 is less than that of the alloy treated with T5 during the aging time, but the difference in conductivity between the two treatments reduced with the increase of the aging time. In figure 5(b), the electrical conductivity increased first and then reduced with the increase of the pre-aging time. Figure 5(c) compares the conductivity of alloys in the state of T5 and two-stage aging. It is clear in the figure that the electrical conductivity is improved after two-stage aging. Figure 5(d) shows the electrical conductivity of ZM51 alloys after two-stage aging following solution treatment. As can be seen from the figure, the electrical conductivity of the alloys increased with the increase of the pre-aging time. Figure 5(e) compares the conductivity of alloys in the state of T4+single aging and T4+two-stage aging. Compared with T4+single aging treatment, the conductivity of the alloys treated with T4+two-stage aging was higher at the beginning of aging, but the electrical conductivity of the T4+single aging treated alloys becomes higher than that of the T4+two-stage aging gradually with the increase of the aging time.
According to the Mattiessen rule, the electrical conductivity of the alloys could be determined as follows [13],

$$\rho = \rho_{\text{pure}}(T) + \sum \rho_i C_i + \rho_p$$

where $\rho_{\text{pure}}(T)$ represents the matrix resistivity related to temperature and texture, $\rho_i C_i$ is the sum of the resistivity due to solute atoms in the matrix, and $\rho_p$ represents the precipitation resistivity contributions. Therefore, the changes in the conductivity of the alloys are the result of the combined action of the solute atoms as well as the structure and distribution of the precipitates.
Normally, the existence of crystal defects such as solid solution atoms or impurities, vacancies, dislocations, grain boundaries and interfaces cause interference to periodic potential in pure metal field thereby leading to an increase in the probability of electron scattering [14]. As a result, the conductivity is reduced. It’s noted that the solid solution atoms are the major factors affecting the electrical conductivity of the alloys among these influencing factors, which means that the more solute atoms dissolved, the lower the conductivity, because solute atoms block the movement of conducting electrons in the matrix, increase the scattering density of electrons and reduce the average free path of electrons. After solution treatment, Zn atoms of ZM51 magnesium alloy are dissolved back to obtain supersaturated replacement solid solution. The lattice of Mg matrix is damaged, resulting in serious distortion. The scattering ability of free electrons is enhanced, the average free path of electron motion is reduced, and the electrical conductivity is reduced.

In the process of aging, the solute atoms in matrix precipitate and lead to the decrease of the lattice distortion of the Mg matrix. The conductivity of the alloy increases with the aging time. In the early stage of aging, the matrix is in supersaturated solid solution state causing the evolution. The solute atoms with large power have a fast precipitation rate, and the conductivity of the alloy is rapidly increasing. With the prolonging of the aging time, the solid solubility decreased and the dissolution power of the solute atoms decreased. Hence, the increase rate of the conductivity of the alloys slowed down and became stable.

It can be seen in figure 2 that there are high-density dislocations in the extruded and T5 pre aged alloys, and dislocations can reduce the nucleation potential barrier of the precipitation strengthening phase, which can be used as the nucleation core of the second phase, thus promoting the precipitation of Zn atoms in Mg matrix. Moreover, after solution treatment, the dislocation density of the alloy is reduced, but the supersaturation of Zn atoms in Mg matrix increases, and the precipitation dynamics increases, which is also conducive to the precipitation of Zn atoms from the matrix. In Figure 5 (a), the increase rate of conductivity of T5 treated alloy is higher than that of T6 treated alloy in early aging stage, which proves that high density dislocation can accelerate the precipitation of solute atoms more than supersaturation of solute atoms in matrix.

Mg-Zn-based alloys will form the GP zones which are coherent with the matrix in the low temperature aging process. The formation of GP zones can cause a greater lattice distortion of the substrate as well as provide heterogeneous nucleation center for the precipitation of the second phases at high temperature, so that the distribution of precipitates is more diffuse and the size is smaller. And the precipitates whose size are smaller than the average free range of electrons will significantly increase the probability of electron scattering, thereby reducing the conductivity, so the conductivity of the alloy will decrease with the volume fraction of precipitates nuclei or GP zones increasing significantly [15]. During two-step aging, the pre-aged G.P. zone is favorable to the formation of fine dispersed second phases, which can reduce the conductivity of the alloy. Therefore, the reason that the conductivity of the alloy treated by pre-aging for 32h is lower than that of the pre-aging for 24h is probably that the alloy formed GP zones with a higher volume fraction and a eutectic relationship with the matrix. Meanwhile, the smaller size of β′ phases which nucleate in the GP zones than the average free range of electrons could be another reason.

In summary, although the solute atom is the main influencing factor of the conductivity of ZM51 alloy, one cannot ignore the influence of defects, such as the second phases and dislocations, on the electrical conductivity. Therefore, the change of the conductivity of the alloy is the solute atom and the second phase. As a result of the combination of crystal defects, the heat treatment state of the alloy is different, and the influence degree of each influencing factor is also different.

4. Conclusion
(1) As the aging time increases, the solute atoms in the alloy matrix are precipitated followed by the decreases of the lattice distortion of the matrix. As a result, the scattering ability of the electrons is weakened, and the conductivity of the alloy is improved.
(2) Compared with the single aging, the two-stage aging can simultaneously improve the alloy conductivity and hardness. During the pre-aging process, the solute atoms are precipitated and the lattice distortion is reduced. And the GP zones which formed during the pre-aging process can provide the heterogeneous nucleation center for the $\beta_1'$ phases during the high temperature aging process thus improving the dispersion of $\beta_1'$ phases and refine them.

(3) The pre-aging time has an effect on the conductivity of the alloy. The conductivity of the pre-aging for 8h, 16h and 24h alloys increases with the increase of the aging time while the conductivity of the pre-aging 32h alloy is less than the pre-aging 24h alloy conductivity. The reason may be that the pre-aging 32h alloy forms GP zones with covalent relationship with the matrix, which simplify the precipitation of the $\beta_1'$ phases and increase the scattering effect on the electrons, resulting in a decrease in conductivity.

(4) The specific electrical conductivity of different heat treatment for ZM51 alloys was in the following sequence, T5 Two-stage aging >T5 single aging > T6 two-stage aging > T6+single aging

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