Effect of heat treatment on microstructure, hardness and electrical conductivity of as-extruded ZK80 Mg alloy

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Abstract: The microstructure, hardness and electrical conductivity of as-extruded ZK80 Mg alloy were tested and analyzed by means of microscope, XRD, electrical conductivity and Rockwell hardness tester. The results show that: as-extruded ZK80 Mg alloy has good strengthening effect, the change trend of hardness and electrical conductivity of the alloy is the same, that is, the hardness and conductivity increase in an oscillatory manner, and then decrease after reaching the peak value. The relationship between hardness and conductivity is \( g = 1.06418h - 52.29795 \), and the experimental fitting effect is good.

1. INTRODUCTION
Mg-Zn-Zr series alloy with high strength, good plasticity and corrosion resistance are one of the most studied wrought alloys. Due to high zinc content, poor heat resistance and high hot cracking tendency, many researchers refine the grains by adding rare earth elements or other alloy elements, and form dispersion strengthening phase with Mg to improve the cast-ability and creep of Mg-Zn-Zr alloys, and then the mechanical properties of the alloy can be improved\textsuperscript{[1-2]}. However, the research on the heat transfer and conductivity of Mg alloy are rare. According to wiedemann-franzlaw: under the condition of not too low temperature, the ratio of conductivity coefficient and thermal conductivity of metals and alloys is directly proportional to temperature, that is, if the temperature is constant, the electrical conductivity of the alloy is proportional to the thermal conductivity. Therefore, the electrical conductivity of the alloy is one of the important characteristics of the thermal conductivity of the alloy\textsuperscript{[3]}. In addition, the conductivity of the alloy is closely related to the stress corrosion resistance of alloy, the stress corrosion resistance of the general alloy increases with the increase of electrical conductivity.
conductivity. Therefore, electrical conductivity is often used as an important index to determine the properties of alloys\[^4\], and the determination of the conductivity is relatively simple than the thermal conductivity and corrosion resistance of the alloy. Therefore, the paper used the extruded ZK80 Mg alloy as the research carrier to study the relationship between the microstructure, hardness and electrical conductivity of the alloy after heat treatment was studied in the paper, which lays a certain experimental foundation for the development of new high-strength heat-resistant and corrosion-resistant wrought Mg alloy.

2. EXPERIMENTAL MATERIALS AND METHOD

Using pure Mg ingot, Zn ingot, Mg-30% Zr master alloy and common Mn as raw materials, the semi-continuous casting ingot of ZK80 Mg alloy was obtained by melting in power frequency furnace, refining with Ar 10L/min for 15min, using SF\(_6\)+N\(_2\) as gas protection, cooled to 740°C and standing for 40min. After the ingot was removed from the surface of the ingot to obtain the size of Ф112mm×125mm, it was treated by solution treatment at 400°C×12h, and then extruded into a plate-shaped section with a cross-section of 100mm×6mm on an 800t extruder. The extrusion temperature was 385°C, the extrusion ratio was 16:1, and the extrusion speed was 17m/s. The composition of as-extruded ZK80 Mg alloy is shown in Tab.1.

The as-extruded ZK80 Mg alloy sheets were aged at 160°C, 180°C, 200°C and 220°C for different holding times. After air cooling, the samples of 12mm×12mm×6mm were cut off by wire cutting, and the prepared sample is pre-ground and polished, its is corroded by a mixed solution of picric acid 1.5g + ethanol 25ml + acetic acid 5ml + distilled water 10ml for 3~10s and observe its microstructure, through the Rockwell hardness tester and vortex conductivity meter to determine the hardness and electric conductivity, the relationship between hardness and conductivity was analyzed.

| Table 1 Chemistry composition of alloy |
|---------------------------------------|
|  | Alloy | Zn   | Zr   | Mn   | Fe   | Si   | Ni   | Cu   |
|---|-------|------|------|------|------|------|------|------|
| ZK80 | 7.470 | 0.4498 | 0.006 | 0.002 | 1 | 0.0037 | 0.0009 | 0.001 |

3. EXPERIMENTAL RESULTS AND ANALYSIS

3.1 Microstructure and hardness curve

Fig.1 shows the microstructure of the original magnesium alloy. It can be seen from the figure that refinement of dynamic recrystallization refinement occurs at the maximum deformation position during extrusion deformation, which indicated that the alloy has obvious dynamic recrystallization. In addition, obvious precipitation of the second phase can be observed in the extrusion direction. Fig.1(a), a large number of twin microstructures and coarse non-recrystallized deformed grains are distributed along the extrusion direction, and fine grains are distributed between the twin microstructures equiaxed grains; Fig.1(b) shows the microstructure of transverse (perpendicular to the extrusion direction) section of extruded ZK80 Mg alloy, which has no fiber streamline characteristics, mainly consists of equiaxed grains of different sizes and a few of twins. According to reference\[^6-9\], the phase in extruded ZK80 Mg alloy is mainly composed of sheet-like \(\beta\)-MgZn\(_2\) phase and rod \(\beta\)-MgZn phase, as shown in Fig.4(a).

Twining can provide an additional independent slip system in low temperature deformation, which can improve the low-temperature plastic deformation ability of the alloy, and twinning is easy to form where the slip can’t continue\[^10-11\]. The extrusion deformation temperature of ZK80 Mg alloy is relatively low, and the deformation speed is fast, which is easy to cause the accumulation of slip, increase the local internal stress of the alloy. According to the relevant literature\[^11\], twins are preferentially formed on large-size grains, and the larger the grains, the easier it is to produce twins, therefore, in as-extruded ZK80 Mg alloy, it is easy to form small equiaxed grains on the deformed large grains.
The general relationship between hardness and strength is $\sigma_b = K \cdot HB$, that is, the hardness is proportional to the strength, and $K$ varies with the metal and its morphology\cite{5}. The morphology, size, and number of the second precipitated phase in the alloy have direct impact on the hardness of the alloy, and the change process of hardness is reflection of the dynamic process of precipitation strengthening of aging strengthened alloy. Therefore, the hardness reflects the microstructure and strength of ZK80 Mg alloy to a certain extent. Fig. 2 shows the hardness change curve of as-extruded ZK80 Mg alloy after different artificial heat treatment conditions. It can be seen from the Fig. 2 that with the prolongation of aging holding time, the hardness curve of as-extruded ZK80 Mg alloy rises in an oscillatory manner, when the artificial heat treatment process is 180°C×12h, the peak hardness is 78.4HRE, which is 16.3% higher than that of the original sample; the peak hardness of the four process first increases with the increase of temperature, and then decreases rapidly after reaching the peak hardness of 78.4HRE, such as Fig.3.

In the early aging stage of Mg-Zn based alloy, the fine rod-like $\beta_1$-MgZn phase is first precipitated\cite{5}. With the aging time increasing, the rod-like $\beta_1$-MgZn precipitated phase transforms into a flaky C14-MgZn$_2$ Laves($\beta_2$-MgZn$_2$) phase\cite{11-12}, the size of the lamellar precipitates is relatively large, which has a good coherent relationship with the Mg matrix. In the Mg-Zn series alloys with certain twins, it is expected to obtain more the basal disc-shaped $\beta_2$-MgZn$_2$ phase with obvious hardening effect instead of the rod-shaped $\beta_1$-MgZn phase to improve the strength of the twinned magnesium alloy in a specific direction after aging treatment. The aging strengthening effect of Mg-Zn alloy depends on the amount and morphology of precipitates, and the quantity of precipitates and morphology depend on the aging holding time, so it is very important to select a reasonable aging holding time. With the increase of aging holding time, the amount of $\beta_2$-MgZn$_2$ phase increases rapidly, while $\beta_1$-MgZn phase is almost invisible. After aging holding time reaches 12h, $\beta_1$-MgZn phase begins to precipitate, while $\beta_2$-MgZn$_2$ phase decreases correspondingly, and the hardness of the alloy reaches the peak. Therefore, it is preliminarily judged that the best heat treatment process of extruded ZK80 Mg alloy is 180°C×12h.
Fig. 2 Hardness curves of ZK80 alloy under different aging conditions

Fig. 3 shows the comparison of peak hardness of ZK80 Mg alloy under different aging conditions. After aging heat treatment at 200℃ and 220℃, the peak hardness is lower. According to relevant research\textsuperscript{[11]}, no G.P. zone was found in Mg-Zn Alloy during aging treatment at 200℃ and 220℃, and the main precipitation phase is c-axis rod-like $\beta_{-}$ MgZn phase, and its strengthening effect of the alloy was weak; however, during the aging process at 160℃, due to the low temperature and insufficient precipitation power, the aging time for peak hardness was longer, and the precipitation $\beta_{-}$ MgZn\textsubscript{2} phase, which has a good coherent relationship with the matrix, was less precipitated, causing the peak hardness of the alloy to be lower than that of 180℃×12h aging process.

Fig. 3 Comparison of peak hardness of different aging processes

Fig. 4 XRD spectrum of as-extruded ZK80 alloy

(a) as-extruded ZK80; (b) 180℃×12h

The microstructure analysis of magnesium alloy samples with the best heat treatment process (180℃×12h) shows that the grains in longitudinal section microstructure are distributed along the extrusion direction, and the direction has not changed obviously, but twin microstructures have no been observed in the longitudinal section, the grains are obviously with equiaxed large grains in the direction of extrusion, and a large number small equiaxed grains are distributed along the extrusion direction, as shown in Fig. 5(a), at the same time, a large amount of fine black phase can be seen along the extrusion
direction, while the microstructure of cross section is relatively uniform equiaxed crystal, and only a small amount of twin microstructure is distributed, as shown in Fig. 5(b). The main reason is that the energy of twin grain boundary is higher than that of the matrix, which can provide nucleation energy for the precipitation of the second phase. Therefore, the second phase precipitates near the twins along the extrusion direction, and the equiaxed grains are formed on the twin grain boundary. According to the XRD analysis in Fig. 4(b), after aging heat treatment at 180°C×12h, the composition of the phase in the alloy does not change, but the number and intensity of β1-MgZn2 peak phase increases significantly, and the number of β1-MgZn phase decreases obviously, which indicates that β1-MgZn2 precipitates phase and β1-MgZn phase dissolves in the alloy. In Fig. 5(a), a large number of black fine particles along the extrusion direction are corresponding to β1-MgZn2 phase, while β1-MgZn2 plays an important role in strengthening the alloy. Hardening [10-11], so the hardness of the alloy is obviously improved, which indicates that ZK80 Mg alloy has good aging strengthening alloy.

Fig. 5 Microstructure after artificial aging heat treatment at 180°C×12h
(a) the longitudinal section;  (b) the transverse cross

3.2 Discussion and analysis of the relationship between hardness and conductivity
Fig. 6 shows the curve of the relationship between electrical conductivity and hardness of ZK80 Mg alloy with the increase of the aging heat treatment time. It can be seen from the figure that the hardness and conductivity of the alloy show the same change trend with the extension of time. When the hardness reaches the maximum value, the electrical conductivity also reaches the maximum value (33.1% IACS), which is 26.3% higher than that of the original sample. In conclusion, 180°C×12h is the best aging heat treatment process.

Fig. 6 Relationship between hardness and electrical conductivity of extruded ZK80 Mg alloy
According to Pearson correlation coefficient, the statistical formula correlation between hardness and electrical conductivity of as-extruded ZK80 Mg alloy is as follows:
The electrical conductivity is not only proportional to the thermal conductivity, but also an important characterization of alloy corrosion resistance, that is, when the electrical conductivity of alloy is increased, the corrosion resistance of the alloy will be improved. Therefore, the electrical conductivity is considered as one of the important evaluation indexes to evaluate the comprehensive performance of the alloy\textsuperscript{[13]}. The electrical conductivity of the alloy is closely related to the scattering degree of electron conduction, in which the scattering degree of electron conduction is affected by the factors such as matrix, grain boundary, dislocation and hole, morphology and quantity of solid solution atoms and the second phase, and the solid solution atom has the greatest influence. The solid solution atom precipitates form the matrix, and the electrical conductivity of the alloy is significantly improved\textsuperscript{[3]}. The main factors affecting the electrical conductivity during aging are\textsuperscript{[3,4,13]}: 1) the precipitation of solid solution atoms in the matrix leads to the decrease of solid solution concentration, the reduction of lattice distortion, and the weakening of electron scattering, which leads to the increase of electrical conductivity; 2) during aging, the second phase particles precipitate form the supersaturated solid solution, and the single-phase alloy microstruture changes into the multiphase microstructure, which enhances the additional scattering effect on electrons and decreases the electrical conductivity. Finally, the change of electrical conductivity of the alloy is caused by combination of two factors.

According to starink model\textsuperscript{[14]}, the conductivity formula of the alloy is as follows:

\[
\frac{1}{\sigma_M(t)} = \rho_M(t) = \rho_{M,p} + \sum_{i=1}^{n} r_i x_i(t)
\]

where \(\sigma_M(t)\) is the matrix conductivity of the alloy; \(\rho_M(t)\) is the resistivity of the matrix phase; \(\rho_{M,p}\) is the resistivity of the pure metal; \(n\) is the amount of alloy elements; \(x_i\) is the concentration of alloy element \(i\) in the matrix (precipitation phase may be precipitated with the change of time); \(r_i\) is a constant; \(t\) is the aging holding time.
As-extruded ZK80 Mg alloy alloy is mainly composed of Zn and Zr, and the content of Zr is less, which mainly refines the grain size of ZK80 Mg alloy, and the effect on electrical conductivity of ZK80 alloy can be ignored. After artificial aging heat treatment, with the increase of aging holding time, there are a large number of black fine dots precipitated in the grains and grain boundaries of the extruded ZK80 Mg alloy, that is, the amount of disk $\beta'_2$-MgZn$_2$ phase increases gradually, while the rod-like $\beta$-MgZn decreases gradually, which makes Zn in the alloy consumed, reduces the concentration of solid solution to a certain extent, reduces the degree of lattice distortion of the matrix, and then reduces the degree of electron scattering, reduces the hindrances of electron conduction, and the conductivity of the extruded ZK80 Mg alloy has been improved. However, with the increase of temperature (200℃, 220℃), no G.P. was found, at the same time, the c-axis rod-like microstructure $\beta'_3$-MgZn$_2$ phase, which is weakly bonded to the matrix, precipitated and the number of $\beta'_1$-MgZn$_2$ phases with good coherent relationship with the matrix decreased, which led to Zn consumed, so that the concentration of Zn element has a certain increase, which makes the electron conduction increase, therefore, the hardness of the alloy decreases while the electrical conductivity also decreases, that is, the change trend is same. When the aging heat treatment temperature (160℃) is low, the atom diffusion ability is weak, and the second precipitation power is insufficient resulting in the second phase precipitation is not enough, leading to a longer time for the hardness peak value, while the electrical conductivity improvement is not obvious. Therefore, combined with aging hardness curve and electrical conductivity analysis, it can be further determined that the best heat treatment process of ZK80 Mg alloy is 180℃×12h.

4. CONCLUSION
1) There is a strong linear correlation between hardness and electrical conductivity of extruded ZK80 Mg alloy. The linear relationship is $g=1.06418h-52.29795$, which means that the change trend of hardness and conductivity is the same. With the increase of artificial aging holding time, the hardness and conductivity of the alloy first increase, then reach the peak value and then decrease;
2) After aging at 180℃×12h, the hardness and electrical conductivity of the alloy are increased by 16.3% and 26.3%, respectively, indicating that the extruded ZK80 Mg alloy has good aging strengthening property, and this process is determined to be the best heat treatment process.

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