Effect of Solution Treatment on Microstructure and Corrosion Resistance of AZ91HP Magnesium Alloy

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Abstract. The microstructure and corrosion resistance of AZ91HP magnesium alloy after different solution treatment were studied emphatically by means of optical microscopy (OM), electrochemical polarization curve and 3.5% NaCl solution immersion and other analytical methods. The results show that the coarse β-Mg17Al12 phase with continuous reticular distribution dissolves at the grain boundary after the as-cast AZ91HP magnesium alloy through solution treatment at 415°C for 24h with air-cooling, the Al element diffuses more adequate in the α-Mg matrix and the content of β-Mg17Al12 is much more. When cooling in water, because of the rapid cooling rate, the amount of Al elements in the matrix of α-Mg is less, and the formation of β-Mg17Al12 is less; the grain size of the magnesium alloy by composite solution treated is significantly reduced. After composite solid solution treatment at 410°C, a small amount of undissolved β phase still exists at the grain boundaries of α-Mg. When the temperature of the composite solution rose to 415°C, the phase of β-Mg17Al12 at the grain boundary was completely dissolved; the corrosion resistance of solid solution AZ91HP magnesium alloy is better than that of as-cast alloy.

1. Introduction
Magnesium alloy is the lightest metal structure material, known for its low density, high specific strength, specific stiffness, good shock resistance, cutting processability and electromagnetic shielding, and widely used in aerospace, national defense, automobile, electronics, transportation and so on, but due to the standard electrode potential of Magnesium alloy is low (-2.37 V SHE), chemical properties is lively, the Magnesium alloy surface is hard to form stable protective film, so prone to be corroded and limits its application; Therefore, to improve the corrosion resistance of AZ91 magnesium alloy has been the focus. Of domestic and foreign scholars research.

This experiment used the method of solid solution and composite solid solution, αphase plays an important role in the corrosion of AZ91 Magnesium alloy, and its corrosion resistance determines the corrosion behavior of the alloy. The micro-composition of α phase is the key of its corrosion behavior, under the condition of different process, aluminum elements distribution is not exactly the same, the speed of solidification is faster, the segregation of aluminum is larger and the distribution of aluminum is more uneven; Because of the different aluminum content, caused the different corrosion behavior[1-9]; Therefore it is necessary to analyze the solidification process, content, form and distribution, and to achieve the goal of improving corrosion resistance of Magnesium alloy.

2. Experimental
The test using AZ91HP magnesium alloy as the research object, its chemical composition are shown in Table 1. The test sample is taken from the concentric circle of the ingot. In order to ensure the
consistency of the original sample, the magnesium alloy was cutted into 15×10×5mm sample. Solution treatment was performed at 415°C for 24h, with air-cooling and water-cooling to room temperature; Composite solution treatment was performed at 415°C for 24h with the furnace cooling, and then were performed at 410°C and 415°C for 20h, with air-cooling to room temperature; The polished samples were immersed into citric acid solution to about 8~10s for corrosion. Using Gx71 Olympus metallographic microscope to observe the Optical microstructure and corrosion microstructure; the specimens were immersed in 3.5 wt.% NaCl solution, exposed to laboratory conditions at a temperature of 25°C, and finally put the corroded sample into the chromic acid solution to remove the corrosion products. Afterwards the specimens were quickly washed with distilled water, dried using a hair dryer. Polarization curve was tested by using cs double-cell electrochemical workstation in 3.5 wt.% NaCl solution. Each heat treatment parameter used three samples. One sample was used to observe the OM, one sample was used to observe the corroded morphology and one sample was used to test the polarization curve.

Table 1. Chemical composition of cast AZ91 magnesium alloy (wt%)

|       | Al  | Zn  | Mn  | Fe  | Si  | Cu  | Mg  |
|-------|-----|-----|-----|-----|-----|-----|-----|
|       | 8.95–9.75 | 0.35–0.1 | 0.15–0.5 | 0.0003 | 0.022 | 0.021 |allowance |

3. Results and discussion

Figure 1 shows the AZ91HP magnesium alloy as-cast, Solid solution and composite solid solution state, As can be seen from Fig. 1 (a), the as-cast AZ91HP magnesium alloy consisted of two phases, α-Mg and β-Mg17Al12. The gray-white microstructure is α-Mg matrix and the black microstructure is β-Mg17Al12 phase. β-Mg17Al12 phase is discontinuous and netted, distributed at the grain boundary, and a small amount of β-Mg17Al12 is granular distributed in the grain. Fig.1 (b) (c) shows a microstructural photo of AZ91HP magnesium alloy by solid solution with air-cooled and water-cooled, From Figure 1 (b) (c) we can see that the solution treatment basically eliminates dendritic segregation phenomenon, most of the β second phase at the grain boundary has been dissolved, and some of the β phase precipitated from the grain boundary of the α-Mg matrix. Due to the different cooling rates after solution treatment, the precipitation amount of β-Mg17Al12 phase is also different, the rate of water cooling is faster, the precipitation amount of Al in the solution and α-Mg matrix is less, the formation of β-Mg17Al12 phase is less, the rate of air cooling is slower, Al elements diffusion in the α-Mg matrix is more adequate, the formation of β-Mg17Al12 phase more. Fig.1 (d) (e) shows the microstructure of AZ91HP magnesium alloy after composite solution treatment at different temperatures. Compared with the solution treatment, the grain size of AZ91HP magnesium alloy after composite solution treatment is obviously reduced. The AZ91HP magnesium alloy after the composite solution-alloyed at 410°C, a small amount of undisolved β phase still exists in the α-Mg grain boundaries and the number is large. After the AZ91HP magnesium alloy was composite solution-treated at 415°C, the β-Mg17Al12 the phase is almost completely dissolved.
(a) as-cast (b) 415°C×24 h air cooling (c) 415°C×24 h water cooling (d) 415°C×24 h (cooling in the furnace) + 410°C×10 h (air cooling) (e) 415°C×24 h (cooling in the furnace) + 415°C×10 h (air cooling)

Figure 1. AZ91HP magnesium alloy as-cast, solution and composite solid solution state

Figure 2 shows the surface morphology of as-cast AZ91HP magnesium alloy after immersion in 3.5% NaCl solution for 240h after solution treatment and composite solution treatment. Compared with solution treatment, it can be seen that the corrosion resistance of AZ91HP magnesium alloy after composite solution treatment is improved. Figure 2 (b) (c) is the surface morphology of the magnesium alloy after immersion in 3.5% NaCl solution for 240h after solution-air-cooling and solution-cooling treatment. The surface corrosion pit of the magnesium alloy under solid solution and air cooled magnesium alloy is shallow, which is mainly pitting, and the surface of the magnesium alloy under solid solution and water cooled has a larger corrosion pit and is connected to pieces. Figure 2 (d) (e) shows the surface morphology of magnesium alloy after soaking in 3.5% NaCl solution for 240 h after composite aging treatment. The surface of the composite solid solution 410°C magnesium alloy is in uniform corrosion, Surface corrosion pit of the composite solid solution 410°C magnesium alloy is small and densely connected into pieces. The corrosion resistance of the magnesium alloy is related to the content of the β-Mg17Al12 phase. The difference in the content of the β-Mg17Al12 phase determines the difference in the corrosion resistance of the magnesium alloy. When the content of the β-Mg17Al12 phase is relatively small, the corrosion resistance of magnesium alloy is poor. For example, the content of the β-Mg17Al12 phase in the microstructure of the cast AZ91HP magnesium alloy is very small, and it is distributed along the grain boundary. Because the content of its β-Mg17Al12 phase is relatively small, during the corrosion process, the β-Mg17Al12 phase is the cathode of the corroded primary battery, which will accelerate the corrosion of matrix -Mg, so the corrosion resistance of as cast AZ91HP magnesium alloy is very poor. When the content of the β-Mg17Al12 phase is relatively large, during the corrosion process, the β-Mg17Al12 phase will play a mechanical role in protecting the matrix and isolate the matrix structure, thus inhibiting the corrosion of magnesium alloy. When the content of the β-Mg17Al12 phase is too high, the corrosion of the -Mg phase will cause dissolution of the α-Mg17Al12 phase on the magnesium alloy substrate, so that the β-Mg17Al12 phase will fall off from the surface of the magnesium alloy. It aggravates the corrosion of magnesium alloy.
Figure 2. Surface morphology of cast AZ91HP magnesium alloy after solid solution and composite solution treatment in 3.5% NaCl solution for 240h

Figure 3 is the dynamic potential polarization curve of AZ91HP magnesium alloy after different heat treatment processes; It is shown from the diagram that the self-corrosion potential of the cast AZ91HP magnesium alloy is -1.521V, and the self-corrosion potential of the magnesium alloy treated by the composite solution at 410°C is -1.473V; The self-corrosion potential of magnesium alloy treated by 415°C composite solid solution is -1.526V. The self-corrosion potential of magnesium alloy after solid solution air cooling is -1.533V, and the self-corrosion potential of magnesium alloy after solid solution water-cooling is -1.546V. The self-corrosion potential of magnesium alloys from large to small is composite solution at 410°C, as cast, composite solution at 415°C, air cooling and water cooling; Therefore, the self-corrosion potential of the composite solution at 410°C is the highest and its corrosion resistance is the best, which is in accordance with the results obtained from Figure 1 and Figure 2.

Figure 3. The electrochemical polarization curve of AZ91HP magnesium alloys of in 3.5wt. % NaCl aqueous solution
4. Conclusions
The as-cast AZ91 magnesium alloy was composed of α-Mg and the divorced black β-Mg17Al12 phases, and the latter were precipitated and irregularly distributed in α-Mg matrix with network during the non-equilibrium crystallizing processes. After the AZ91HP magnesium alloy through solution treatment at 415°C for 24 hours, because of the different cooling rate, the air-cooling has more β-Mg17Al12 than the water cooling. The grain size of magnesium alloy treated by the composite solution is significantly reduced than solid solution. After composite solid solution treatment at 410°C, a small amount of undissolved β phase still exists at the grain boundaries of α-Mg. When the temperature of the composite solution rose to 415°C, the phase of β-Mg17Al12 at the grain boundary was completely dissolved; the corrosion resistance of solid solution AZ91HP magnesium alloy is better than that of as-cast alloy.

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6. References
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