Influence of the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase morphology on the corrosion properties of AZ91HP magnesium alloy

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Abstract: The morphology of $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase and corrosion behavior of AZ91HP magnesium alloy after spheroidizing treatment were investigated by optical microscope, electrochemical and immersion tests in 3.5% NaCl at 25°C. The results show that the coarse divorced eutectic phase of AZ91HP cast magnesium alloy dissolve into Mg matrix during the isothermal process at 415°C, and the lameller $\beta$ phase precipitated from magnesium solid solution as perlite-type precipitation during the slowly cooling. Next, the spheroidizing treatment at different temperatures for 20h was carried out, and the lameller $\beta$ phase were spheroidizing by dissolved themselves. After spheroidizing treatment at 300°C for 20h, many small granular $\beta$ phase are scattering within the magnesium matrix. The corrosion properties of AZ91HP magnesium alloy in 3.5% NaCl decreased obviously after spheroidizing treatment, the polarization measurement of the alloy can be up to -1.412V from -1.56V of the cast. The $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase act as a corrosion barrier and hinder corrosion propagation, if the second phase is in the form of a spherical morphology.

1. Introduction
Magnesium alloys being recognized as green materials in the 21st were widely applied in traffic transport, electronic communications, aerospace, national defense and so on, due to their characteristics of lightness, high specific strength and specific, easily recycled, environmentally friendly. However, the chemical properties of magnesium lively and very easily oxidized in the air, the corrosion potential of magnesium and its alloys are very low, it can't protect the matrix and easily prone to serious corrosion, has limited their further application [1-5]; So it is meaningful to explore the way of improving the corrosion resistance of magnesium alloy. This study can be helpful to improve the property and application of magnesium alloy.

In the past few decades, there are many studies about the effects of phase composition on the corrosion behavior of magnesium alloys, $\beta$ phase is the strengthening phase, it has stronger corrosion resistance than $\alpha$ phase, it plays two different roles in corrosion: (1) as cathode of corrosion cell, accelerating corrosion; (2) as a barrier of anode reaction, inhibiting corrosion; the different roles of $\beta$ phase depends on the content of $\beta$ phase [6]. Therefore, in this paper, by studying the effect of spheroidizing temperature on AZ91HP magnesium alloy corrosion resistance, the corrosion resistance of magnesium alloys can be improved by getting small $\alpha$ phase and the appropriate content of $\beta$ phase.

2. Experimental
This paper makes AZ91HP magnesium alloy as the research object, its chemical compositions are shown in table 1. The as-cast magnesium alloy was cutted into 15×10×5mm samples; Homogenized
treatment was performed at 415°C for 24h with furnace cooling to room temperature, then through different spheroidizing treatment. The polished samples were immersed into the mixed solution of glycerin, hydrochloric acid, nitric acid and acetic acid about 8~10s for corrosion. Optical microstructure and corrosion microstructure were analyzed with OLYMPUS GX71 metallographic microscope.(OM).The specimens were weighed for the original mass. In the process of Corrosion tests, the specimens were immersed in 3.5 wt.% NaCl solution, exposed to laboratory conditions at a temperature of 25°C. After the corrosion tests, the corroded specimens were photographed and then immersed into a ammonium solution at room temperature to remove the corrosion products. Afterwards the specimens were quickly washed with distilled water, dried using a hair dryer. At room temperature, polarization curve was tested by using cs double-cell electrochemical workstation in 3.5 wt.% NaCl solution.

### Table1 Chemical compositions of AZ91HP samples (wt.%)  

|    | Al   | Zn  | Mn   | Ni  | Cu  | Ca  | Mg  |
|----|------|-----|------|-----|-----|-----|-----|
|    | 8.005| 0.593| 0.199| 0.001| 0.001| 0.001| Balance |

3. **Results and Discussion**

The microstructure of the as-cast AZ91HP alloy and spheroidized at different temperature for 20h are shown in Fig.1. It is found that AZ91HP magnesium alloy had a two phase microstructure consisting of α-Mg matrix, divorced eutectic β-Mg₁₇Al₁₂ phases along the α grain boundaries in Fig.1(a). When the samples were spheroidized to various temperatures for 20h, the number and morphology of the second phase has changed greatly, the second phase were more and smaller. The layer second phase gradually melt with spheroidizing temperature increasing. Finally the second phase were diffusely distributed in the α-Mg matrix, and the structure morphology of the second phase has changed from the original layer to the granular. When the spheroidizing temperature was at 270°C, it can be seen from Fig.1(b) that the layer second phase has mostly remained. Only few β phase fused into short rod,β phase showed short rod or granular in the α-Mg matrix with the increasing spheroidizing temperature, when the spheroidizing temperature was at 290°C (Fig.1(d)). Fig.1(e) shows that the layer second phase did not exist, and the granular second phase increased when the spheroidizing temperature was at 300°C. It can be observed from Fig.1(f) that the second phase was diffusely distributed in the α-Mg matrix and appeared granular structure after spheroidizing treatment at 310°C.

Fig.2 shows the corrosion morphology of AZ91HP alloy treated at different spheroidizing temperature immersing in 3.5wt.% NaCl solution for different time. The surface corrosion degree of the as-cast magnesium alloy was more serious than that of spheroidized samples, so the spheroidizing treatment improved markedly the corrosion resistance of AZ91HP magnesium alloy. It can be seen from Fig.2(a) that there was no obvious corrosion pit on the sample surface, but the overall sample surface was pitted corrosion, when the samples were immersed at 270°C for 2h; when the immersion
time increased to 96h, the surface corrosion degree of AZ91HP magnesium alloy aggravated gradually, corrosion points got together and gradually got bigger, and the corrosion went deeply from the samples surface to the internal, the corrosion morphology changed from the pitting corrosion to honeycomb (Fig.2(b)). Compared with the morphology of spheroidizing temperature at 270°C and 310°C, the corrosion degree of magnesium alloy was less when the spheroidizing temperature was at 290°C (Fig.2(c)(d)). Above phenomenon is related to the β phase content, the early granular β phase content is less, β phase acted as a cathode and accelerated the dissolution of magnesium matrix; granular β phase content increased at 290°C, the magnesium matrix was isolated, the corrosion product increased and the corrosion degree reduced with the increasing of corrosion time; when spheroidizing temperature added to 310°C (Fig.2(e)(f)), particle content was more, with the extension corrosion time, the magnesium substrate has been eroding, made β phase lost support and fell off, accelerated the corrosion of magnesium alloys.

The electrochemical polarization curve of the AZ91HP magnesium alloys in 3.5wt.% NaCl aqueous solution was shown in Fig.3. The corrosion potential: 300°C > 290°C > 310°C > 270°C > 280°C > the as-cast. It can be seen that the best corrosion resistance was at 300°C; the corrosion current: the as-cast > 270°C > 310°C > 280°C > 300°C > 290°C. It can be seen that the best corrosion resistance was at 290°C. Although the results of the corrosion resistance were different, the corrosion potential at 300°C were greater than that at 290°C. The 300°C measured corrosion current was a little higher than the 290°C measured corrosion current. Comprehensive analysis shows that the spheroidizing temperature at 300°C has good corrosion resistance.
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. In the spheroidizing process, with the increasing of spheroidizing temperature, the layer β second phase continuously melted. The microstructure form of β phase changed from the original layer to the granular, after spheroidizing treatment at 300°C for 20h, many small granular β phase are scattering within the magnesium matrix. The corrosion resistance of AZ91HP magnesium alloy increased firstly and then decreased with the increasing of spheroidizing temperature; When the spheroidizing temperature was at 300°C, the content and form of the β phase was the most appropriate, and also showed the optimum corrosion resistance.

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