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Corrosion behaviour of Mg–Gd–Y–Zn–Ag alloy components with different sizes after cooling

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Abstract: The corrosion behaviour of Mg=6Gd=3Y=1Zn=0.3Ag (wt.%) alloy components with different sizes after cooling was investigated. The alloys in the small components (SC) cooled fast, which were composed of α -Mg matrix and coarse long-period stacking ordered (LPSO) phases. The alloys in the large components (LC) cooled slowly, and there were thin lamellar LPSO phases precipitating inside the grains, except for α -Mg matrix and coarse LPSO phases. The hydrogen evolution test revealed that the corrosion rate of LC sample was higher than that of SC sample. Electrochemical impedance spectroscopy (EIS) test showed that the surface film on LC alloys provided worse protection. The corrosion morphologies indicated that the precipitation of the thin lamellar LPSO phases in LC sample caused severe micro-galvanic corrosion, which accelerated the rupture of the surface film.

Key words: Mg-Gd-Y-Zn-Ag alloy; cooling process; long-period stacking ordered (LPSO) phase; surface film; micro-galvanic corrosion

1 Introduction

The demand for high energy efficiency and low emission vehicles is rising with the global energy crisis and environmental pollution becoming more and more serious, and the lightweight design is an efficient way to achieve this demand. The consumption of magnesium (Mg) alloys as the lightest structure metal in the vehicle industry steadily has increased in recent years, and the application in the automobile industry has also developed from small components, such as steering wheels, steering column parts and instrument panels to large body parts [1-3]. Compared with the small components, Mg in large components might exhibit different cooling processes. Mg in small components might cool down to room temperature within dozens of minutes, and the microstructure at high temperature might be still maintained during the process. However, the same cooling process takes more than ten hours for the large components, and the precipitation would occur due to the decomposition of supersaturate Mg matrix during the period. The properties of Mg alloys are also affected by the different microstructures. Thus, the research on the effect of cooling processes is beneficial to the development of high-performance Mg alloys.

Mg–RE–Zn alloy with long-period stacking ordered (LPSO) phases is a kind of magnesium alloy with high mechanical properties [4–7]. The addition of silver (Ag) to Mg–RE–Zn alloy induced the additional precipitation or segregation of Ag atoms at the interfaces, which enhanced the age-hardening response and further improved the mechanical properties of alloy [8–12]. LPSO phases were also observed in Mg–RE–Zn–Ag alloys [8]. Thus, the variation in LPSO phases affects the property of the alloys. YAMASAKI et al [13] found that the precipitation of LPSO phases was observed in the Mg–Gd–Zn alloys after

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aging at 400 °C for 10 h. LIU et al [14] found that lamellar 14H phase was formed in the α -Mg matrix during the high temperature annealing at 773 K. BI et al [15] also found that there was LPSO precipitation in homogenized Mg–Dy–Zn alloys with low cooling rate (2 °C/min). These studies indicate that cooling processes affect the precipitation of LPSO phases in Mg–RE–Zn alloys.

Numerous previous studies indicated that the second phases played an important role in the corrosion behavior of magnesium alloys [16,17], which exhibited the double effects on the corrosion property. SONG et al [18-20] reported that the corrosion mechanism of Mg-Al alloys was influenced by the volume fraction and distribution of β -phase (Mg₁₇Al₁₂). When the volume fraction of β -phase was low, the phase formed discontinuously in the α -Mg grain boundary region, which acted as cathode and accelerated the galvanic the degradation of α -Mg matrix. In contrast, the β -phase with high volume fraction formed the interconnected network composed of the eutectic phases, which acted as the barrier and inhibited the propagation of corrosion on the α -Mg matrix. Similar phenomena were also observed in other Mg alloys [21–23]. The volume fraction and morphology of second phases have great influence on the corrosion resistance of Mg alloys. LPSO phases as other second phases showed the complex effects on corrosion resistance due to the difference in the volume fraction, morphology and distribution. In general, the existence of LPSO phases accelerated the dissolution of Mg matrix by causing the micro-galvanic corrosion [24-26]. However, some recent studies presented the opposite results. ZHANG et al [27] found that the Mg-11.3Gd-2.5Zn-0.7Zr (wt.%) alloy with LPSO phases exhibited a better corrosion resistance than Mg-10.2Gd-3.3Y-0.6Zr (wt.%) alloy without LPSO phase. PENG et al [28] reported that the 14H-LPSO phase enhanced the corrosion resistance of Mg-2Dy-0.5Zn (at.%) alloy through improving remediation ability. The influences of LPSO phases on the corrosion resistance were still unclear, and the micro-mechanism requires more investigation.

Herein, the homogenized Mg-6Gd-3Y-1Zn-0.3Ag (all in wt.% unless specified separately) alloys were cooled with different methods to simulate the cooling process in small and large components. The corrosion behaviour of the two

Mg-6Gd-3Y-1Zn-0.3Ag components in 3.5 wt.% sodium chloride (NaCl) solution was investigated. The aims were to investigate the difference in microstructure between small and large Mg-6Gd-3Y-1Zn-0.3Ag components, the corrosion property of the two Mg-6Gd-3Y-1Zn-0.3Ag components, and the influence of cooling processes on the corrosion property and mechanism. It is expected to provide some ideas for the development of Mg-Re-Zn-Ag components with high corrosion resistance.

2 Experimental

2.1 Material preparation

As-cast Mg-6Gd-3Y-1Zn-0.3Ag alloy was prepared by semi-continuous casting method. Pure magnesium (99.96%), pure zinc (99.99%), pure silver (99.96%), magnesium gadolinium master alloy (25% gadolinium) and magnesium yttrium master alloy (25% yttrium) as the raw materials were melted in a resistance furnace under the mixed protective atmosphere of carbon dioxide and sulfur hexafluoride. The composition of the alloy is listed in Table 1.

Table 1 Chemical composition of Mg=6Gd=3Y=1Zn=0.3Ag alloy (wt.%)

Gd	Y	Zn	Ag	Fe	Ni	Cu	Mg
5.8	3.4	0.8	0.3	0.014	0.0023	0.0002	Bal.

The as-cast ingot was cut into $10 \text{ mm} \times 10 \text{ mm} \times 10 \text{ mm}$ blocks, and then the blocks were homogenized at 510 °C for 120 h and cooled by different methods. Subsequently, some blocks were cooled by water quenching cooling method to room temperature to simulate the rapid cooling process (the cooling rate is about 25.5 °C/min) in small components (SC). The other blocks were treated by furnace cooling to room temperature for 12 h to simulate the slow cooling process (the cooling rate is about 0.7 °C/min) in large components (LC).

2.2 Microstructure observation

The phase analysis of Mg-6Gd-3Y-1Zn-0.3Ag alloy was performed using Rigaku D/Max 2500 X-ray diffraction (XRD) with copper target, and the obtained XRD patterns were analyzed by MDI Jade 6.0 software. The morphologies of alloys were observed by a Quantan-200 scanning electron microscopy (SEM). The area fraction of second phases was calculated by image-pro plus software.

The samples for corrosion morphology observation were immersed in 3.5 wt.% NaCl solution at 25 °C for different time, and then dried in a cool air stream. The corrosion morphologies of samples were recorded by the optical microscope and SEM. The severe corrosion areas on samples turned black under the optical microscope, and the fraction of the severe corrosion areas was calculated by the image-pro plus software. Three samples of each alloy (SC and LC) were calculated to minimize the deviations. The morphologies of corrosion products were observed by SEM after spray-gold, and the corrosion morphologies of alloy surface were also observed by SEM after the removal of corrosion products through 180 g/L chromium trioxide solution at 25 °C for 15 min.

2.3 Hydrogen evolution test

The corrosion rate of samples was evaluated by hydrogen evolution test [29]. The cubic samples for the corrosion rate test were successively ground to 1500 grit SiC paper before testing. The samples were encapsulated in epoxy resin with the 10 mm × 10 mm surface exposed to the electrolyte. The samples were immersed in 140 mL of 3.5 wt.% NaCl at 25 °C in beakers. The hydrogen bubbles generated from the sample surfaces were collected by a burette. The decrease of the solution level in the burette reflected the amount of hydrogen generated. The hydrogen levels were recorded every 12 h, and the total immersion time was 48 h. The corrosion rate, $R_{\rm H}$, was evaluated according to the hydrogen evolution rate, $V_{\rm H}$, as follows [29]:

$$R_{\rm H} = 2.15 V_{\rm H}$$
 (1)

Similarly, three samples of each alloy (SC and LC) were tested to minimize the deviations.

2.4 Electrochemical impedance spectroscopy (EIS) test

The electrochemical impedance spectroscopy tests were carried out on the electrochemical workstation (CS310, Wuhan CorrTest Instruments Co., Ltd). The tests were performed in 3.5 wt.% NaCl solution. A typical three-electrode cell was used with a saturated calomel-electrode (SCE) reference electrode, Pt counter electrode and the samples as working electrode. The samples were connected with a wire to one side and encapsulated in epoxy resin with a 1 cm² surface exposed to the electrolyte. The EIS tests were measured at the open circuit potential (OCP) with amplitude of 10 mV. The scan frequency ranged from 100 kHz to 0.01 Hz. The EIS tests were performed on the different samples after immersion for 30 min, 12 and 24 h, respectively.

3 Results

3.1 Microstructure and phase composition

Figure 1 shows the SEM images and XRD patterns of alloys with different cooling processes. As shown in Figs. 1(a, b), coarse gray phases were distributed at the grain boundaries, and fine cubic white phases were randomly distributed both at the grain boundaries and inside the grains. Compared with SC sample, thin lamellar gray phases were precipitated in the grain interior of LC sample (Figs. 1(c, d)). According to the XRD patterns (Fig. 1(e)) and previous works [30,31], the coarse gray phases at grain boundaries and thin lamellar gray phases in the grain interior are LPSO phases. The fine cubic white phases are RE-rich phases, which were not detected in the XRD patterns due to their small volume fractions. Figure 1(f) presents the area fraction of coarse LPSO phases, and the area fractions of coarse LPSO phases are similar in SC and LC samples. These results indicate that the slow cooling process in LC sample leads to the precipitation of thin lamellar LPSO phases in the grain interior.

3.2 Hydrogen evolution

Figure 2 shows the hydrogen evolution test results of SC and LC samples after immersion in 3.5 wt.% NaCl for 48 h. The corrosion rate curves reveal that the corrosion rates of both samples increase with the increase of immersion time, and the corrosion rate of LC sample is higher than that of SC sample.

3.3 EIS test results

The EIS tests were carried out to investigate the effect of cooling process on the corrosion behaviour, and the results are presented in Fig. 3.



Fig. 1 SEM images of Mg-6Gd-3Y-1Zn-0.3Ag sample: (a) SC samples; (b) LC sample; (c) SC sample with high magnification; (d) LC sample with high magnification; (e) XRD patterns of SC and LC samples; (f) Fraction of coarse LPSO phases in both SC and LC samples

The Nyquist plots shapes of SC and LC samples are similar. The Nyquist plots of both samples consisted of two capacitance loops and an inductance loop after immersion for 30 min. The capacitance loop at high frequencies was related to the charge transfer resistance and the electric double layer between the α -Mg matrix and solution [32–35]. The capacitance loop at low frequencies presented the diffusion process in the surface film [35]. The inductance

loop at low frequencies presented the relaxation process of the absorbed monovalent magnesium ions (Mg⁺) [36–38]. The equivalent circuit is shown in Fig. 3(c), where R_s is the solution resistance, R_t is the charge transfer resistance, R_f is the film resistance, constant phase elements (CPE) were used to replace capacitances, CPE_f (Q_f and n_f) is the capacitance of surface film, CPE_{dl} (Q_{dl} and n_{dl}) is the capacitance of double electric layer, R_L is the resistance of absorbed Mg^+ relaxation process, and *L* is the inductance of absorbed Mg^+ relaxation process. After immersion for 12 and 24 h, the Nyquist plots consisted of a capacitance loop at



Fig. 2 Corrosion rate as function of immersion time in 3.5 wt.% NaCl solution

high frequencies and an inductive loop at low frequencies. The capacitance loop at high frequency presented the charge transfer resistance and the double electric layer. The inductive loop presented the relaxation process of absorbed Mg⁺. Thus, the charge transfer process and inductance behaviour were considered in the equivalent circuit (Fig. 3(d)). The similar shapes of Nyquist plots in SC and LC samples indicate that the corrosion processes of both samples are similar.

The fitting results are listed in Table 2. The R_t values of both samples decrease with the increase of immersion time and LC sample have lower R_t values. These tendencies indicate that the corrosion rates of both samples increase with prolonging immersion time, and the corrosion rate of LC sample is higher than that of SC sample. These results are in good agreement with the hydrogen evolution test results.



Fig. 3 EIS results: (a) Nyquist plots for 1 h; (b) Nyquist plots for 12 and 24 h; (c) Equivalent circuit for 1 h; (d) Equivalent circuit for 12 and 24 h

D		SC		LC			
Parameter	30 min	12 h	24 h	30 min	12 h	24 h	
$R_{\rm s}/(\Omega \cdot {\rm cm}^2)$	4	7	7	4	6	6	
$R_{\rm f}/(\Omega \cdot {\rm cm}^2)$	1220			819			
$Q_{\mathrm{f}}/(\Omega^{-1}\cdot\mathrm{cm}^{-2}\cdot\mathrm{s}^{-n})$	1.31×10^{-3}			1.25×10^{-3}			
$n_{ m f}$	0.69			0.70			
$R_{\rm t}/(\Omega \cdot {\rm cm}^2)$	992	312	153	821	244	108	
$Q_{ m dl}/(\Omega^{-1}\cdot m cm^{-2}\cdot m s^{-n})$	1.50×10^{-5}	3.63×10^{-5}	4.10×10^{-5}	1.61×10^{-5}	3.65×10^{-5}	1.2×10^{-4}	
$n_{ m dl}$	0.93	0.93	0.98	0.93	0.93	0.96	
$R_{\rm L}/(\Omega \cdot {\rm cm}^2)$	286	827	85	285	510	92	
$L/(\mathrm{H}\cdot\mathrm{cm}^{-2})$	22091	30	1973	15079	23	1890	
Chi-Squared	0.0015	0.0048	0.011	0.0011	0.0056	0.0043	

Table 2 Fitting results of EIS for SC and LC samples

1296

3.4 Corrosion morphology

The optical images of SC and LC samples as function of immersion time are shown in Figs. 4(a) and (b). The alloy surface was covered by a gray surface film after immersion for 30 min. With the increase of immersion time, the gray areas and black areas were observed on the alloy surface. Figure 4(c) presents the relation between the fraction of black areas and corrosion rates. Two obvious trends were concluded from these results: (1) corrosion rates of both samples increased with the propagation of black areas, which meant that the propagation of black areas deteriorated the corrosion resistance of SC and LC samples; (2) the propagation rate of black areas in LC sample was faster than that in SC sample.

The microscopic corrosion morphologies of both samples were observed by SEM to further understand the effect of cooling process on corrosion behaviour, and the morphologies of surface films are shown in Fig. 5. Both of the Mg matrix and second phases were covered by a smooth surface film after immersion for 30 min (Figs. 5(a) and (b)). After immersion for 24 h, the smooth surface films on the gray areas (Figs. 5(c) and (d)) are similar to the surface film after immersion for 30 min, the morphology of surface film on the black areas exhibits different morphologies. There are many spongy corrosion products on the film surface of the black areas (Figs. 5(e) and (f)), and the rough surface of spongy corrosion products causes the diffuse reflection of light on the surface film, making these areas black under optical microscope. Some cracks were observed on the corrosion product films. SONG et al [39] indicated that these cracks were caused by the effect of vacuum during SEM, which had no connection with the corrosion process. The EDS results are listed in Table 3, and all surface films were enriched with Mg and O elements. There were the peaks for α -Mg and Mg(OH)₂ in the XRD results (Fig. 6). The EDS and XRD results reveal that the main composition of surface film is $Mg(OH)_2$.



Fig. 4 Optical images (a, b) of SC (a) and LC (b) samples after immersion in 3.5 wt.% NaCl solution for different time, and corrosion rate as function of fraction of black areas (c)



Fig. 5 SEM images of SC (a, c, e) and LC (b, d, f) samples showing surface film after immersion for 30 min (a, b), surface film on gray areas after immersion for 24 h (c, d), and surface film on black areas after immersion for 24 h (e, f)

Table 3 EDS results of surface film (at.%)						
Area No.	Mg	0	Gd	Y	Cl	
1	59.5	35.8	2.5	2.2		
2	61.3	33.9	2.9	1.9		
3	60.1	33.8	2.7	2.0	1.4	
4	59.7	34.6	2.7	1.8	1.2	
5	44.9	49.7	0.3	0.2	4.9	
6	31.5	57.2	0.6	2.6	8.2	

Figure 7 presents the corrosion morphologies of the alloy surface after removing the corrosion products. The corrosion pits were detected in the vicinity of second phases in both samples after



Fig. 6 XRD patterns of SC and LC samples after 24 h immersion in 3.5 wt.% NaCl solution



Fig. 7 SEM images of SC (a, c, e) and LC (b, d, f) samples after removal of corrosion products: (a, b) After immersion for 30 min; (c, d) Gray areas after immersion for 24 h; (e, f) Black areas after immersion for 24 h

immersion for 30 min (Figs. 7(a) and (b)). The corrosion pits in SC sample were located in the vicinity of coarse LPSO phases. The corrosion pits in LC sample appeared not only in the vicinity of coarse LPSO phases but also in the vicinity of thin lamellar LPSO phases. These results indicated that LPSO phases caused micro-galvanic corrosion and acted as the galvanic cathode, the micro-galvanic corrosion ruptured the surface films on anodic α -Mg matrixes. Figures 5(c)–(f) show the morphologies after 24 h immersion. The α -Mg matrix on the gray area was slightly corroded, only

shallow corrosion pits were observed, which indicated that the surface films on the gray areas provided effective protection. The α -Mg matrix on black area was severely corroded, which meant that the surface films on the black areas were severely ruptured.

4 Discussion

The hydrogen evolution test and EIS test showed that the corrosion rate of LC sample with slow cooling process is higher than that of SC sample with rapid cooling process. The EIS test also provided information about the influence of surface films on corrosion behaviour. On the basis of literature data [40,41], the interface of Mg alloys was presented as show in Fig. 8. The Mg matrix was covered by a duplex film: a thin compact MgO film contacted with the Mg matrix and a relatively thick porous Mg(OH)₂ film in the outer. The compact MgO film effectively protected the Mg matrix from the corrosion of NaCl solution. The dissolution of Mg matrix only occurred on the film-free areas.

On the film-free areas, the dissolution of Mg matrixes occurred as follows:

$$Mg \xrightarrow{k_1} Mg_{ads}^+ + e^-$$
 (2)

$$Mg_{ads}^{+} \xleftarrow{k_2}{k_{22}} Mg^{2+} + e^{-}$$
 (3)



Fig. 8 Illustration of Mg interface in NaCl solution

The high-frequency capacitive loop corresponded to the charge transfer resistance of Reactions (2) and (3), which was in parallel to the double electric layer capacitance. According to the reaction of Mg dissolution, EIS results can be calculated and simulated by assuming that the adsorbate Mg_{ads}^+ obeys the Langmuir's isotherm and the rate constants of the electrochemical reactions follow the Tafel's law.

The normalized time constant K_i corresponds to its rate constant k_i by

$$K_i = k_i \exp[b_i(\varphi - \varphi_{\text{corr}})] \tag{4}$$

where b_i is the charge transfer coefficient, and φ_{corr} is the corrosion potential obtained at the steady-state in solution.

The charge balance can be expressed as

$$\beta \frac{\mathrm{d}\theta}{\mathrm{d}t} = K_1 \beta (1-\theta) + K_{22} C_{\mathrm{Mg}^{2+}} - K_2 \beta \theta - K_3 \beta \theta \quad (5)$$

where β is the maximum number of adsorption site for Mg⁺_{ads} per unit surface, θ is the surface coverage fraction of Mg⁺_{ads}, $C_{Mg^{2+}}$ is the interfacial concentration of Mg²⁺ in solution. The faradic current density can be expressed as

$$J_{\rm F} = F\gamma [K_1\beta(1-\theta) + K_2\beta\theta - K_{22}C_{\rm Mg^{2+}}]$$
(6)

where *F* is the faraday constant, γ is the fraction of film-free area.

At steady state, the charge transfer resistance R_t can be calculated by [42]

$$R_{t} = \left(\frac{\partial E}{\partial J_{F}}\right)_{ss} = \{F\gamma[b_{1}K_{1}\beta(1-\theta) + b_{2}K_{2}\beta\theta - b_{22}K_{22}C_{Mg^{2+}}]\}^{-1}$$
(7)

The Eq. (7) reveals that the R_t is inversely proportional to the fraction of film-free areas γ . The fitting results show that the R_t in SC and LC samples decreased with the increase of immersion time, which indicated that the protective compact MgO films were gradually ruptured by NaCl solution and the film-free areas propagated during the whole immersion process. The propagation of the film-free areas offered more sites for the dissolution of Mg matrix. As a result, the corrosion rates increased with the propagation of film-free areas. At the same time, the fitting results show that the R_t in LC sample is lower than that in SC sample, which means that the film-free area on LC sample is larger than that on SC sample.

The corrosion morphology confirmed the EIS results. Figure 4 shows that the black area on LC sample is larger than that on SC sample. The SEM images in Fig. 5 and Fig. 7 reveal that the protection performance of surface films on the gray areas is much better than that on the black areas. It can be inferred that the fraction of the film-free areas on the black areas is much higher than that on the gray areas are negligible with respect to the film-free areas on the black areas. The fraction of the film-free areas on the black areas. The fraction of the film-free areas on the gray areas are negligible with respect to the film-free areas on the black areas. The fraction of the film-free areas (γ) can be calculated by

$$\gamma = \gamma_{\rm b} S + \gamma_{\rm g} (1 - S) \approx \gamma_{\rm b} S \tag{8}$$



Fig. 9 Schematic illustration showing influence of thin lamellar LPSO precipitation on surface film

where γ_b is the fraction of film-free areas on the black areas, γ_g is the faction of film-free areas on the gray areas, and *S* is the fraction of black areas. Equation (8) reveals that the fraction of film-free areas is inversely proportional to the fraction of black areas. The larger black areas on LC sample meant that there were larger film-free areas on LC sample than SC sample. Therefore, the surface film of LC sample provided worse protection performance.

The corrosion morphology images in Figs. 7(a) and (b) indicate that the larger film-free areas on LC sample are related to the precipitation of thin lamellar LPSO phases in grain interior, and the influence of thin lamellar LPSO is schematically shown in Fig. 9. Both of the coarse and thin lamellar LPSO phases caused micro-galvanic corrosion and acted as galvanic cathodes. The α -Mg matrix around LPSO phases acted as galvanic anodes. The micro-galvanic corrosion accelerated the rupture of the surface film on anodic sites, which was due to the concentration of chloride ions and acidic pH [43]. The original duplex film was replaced by porous Mg(OH)₂ film [41,44]. More importantly, these small local anodes propagated away from their initiation sites and continually

ruptured the surface film [45,46]. In LC sample, the extra thin lamellar LPSO phases offered more galvanic cathodes. LC sample was subject to severe micro-galvanic corrosion, and there were more local anodes propagating on the LC sample surface, which accelerated the rupture of the surface film. As a result, the corrosion resistance of LC sample is worse than SC sample.

5 Conclusions

(1) The slow cooling process in LC sample leads to the precipitation of thin lamellar LPSO phases in the grain interior.

(2) The corrosion rate of LC sample in 3.5 wt.% NaCl solution is higher than that of SC sample, which is due to the worse protection of surface film in LC sample.

(3) The precipitation of thin lamellar LPSO phases in LC sample causes severe micro-galvanic corrosion, which accelerates the rupture of surface films on LC sample.

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不同尺寸 Mg-Gd-Y-Zn-Ag 镁合金零件冷却后的腐蚀行为

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摘 要:研究不同尺寸的 Mg-6Gd-3Y-1Zn-0.3Ag (质量分数,%)镁合金零件冷却后的腐蚀行为。小型零件冷却 较快,其显微组织由镁基体和粗大的长周期堆垛有序结构(LPSO)相组成。大型零件冷却较慢,其显微组织除镁基 体和粗大的 LPSO 相外,晶粒内部有薄片状 LPSO 相析出。析氢测试结果表明,大型零件的腐蚀速度高于小型零 件。交流阻抗测试显示这是由于大型零件上的表面膜的保护能力较差。通过观察腐蚀后形貌发现,大型零件样品 中晶粒内析出的 LPSO 相诱发更加严重的微区电偶腐蚀,加速样品表面保护膜的破坏。

关键词: Mg-Gd-Y-Zn-Ag 合金; 冷却过程; 长周期堆垛有序(LPSO)相; 表面膜; 微电偶腐蚀

1302