

Preparation of cerium oxide based environment-friendly chemical conversion coating on magnesium alloy with additives

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Abstract: $\text{Ce}(\text{SO}_4)_2\text{--H}_2\text{O}_2$ solution was adopted to prepare a chemical conversion coating on AZ91D magnesium alloy. Additives of $\text{Ni}(\text{NO}_3)_2$ and sodium dodecyl benzene sulfonate were applied to improving the coating formation. SEM, EDS, XRD and GIXD were adopted to study the coating morphology, structure and composition, and the potential change curve in the treating solution was recorded to study the coating growth. Sodium dodecyl benzene sulfonate makes a remarkable improvement in the coating compactness, and shortens the time in the second stage of the coating formation from 5 min to 2 min. Compared to $\text{Ni}(\text{NO}_3)_2$, sodium dodecyl benzene sulfonate makes the more remarkable effect on the corrosion resistance improvement, since it can decrease the current density of corrosion from $7.41 \times 10^{-5} \text{ A/cm}^2$ to $2.20 \times 10^{-5} \text{ A/cm}^2$. The additives of $\text{Ni}(\text{NO}_3)_2$ and sodium dodecyl benzene sulfonate can enhance the Ce content from 18.92% to 22.32% and 25.08% in the coating, respectively. The XRD and GIXD results indicated that all the conversion coating formed in different solutions exhibit amorphous structure.

Key words: magnesium alloys; surface treatment; conversion coating; rare earth; additives

1 Introduction

Magnesium alloy is considered the most promising light material in electronics product and in light-weight engineering applications, aerospace field and automobile industry [1]. In order to improve its corrosion resistance, different surface modification technologies were adopted, including chemical conversion, anodic oxidation, micro-arc oxidation, ion implantation, electroless plating and electroplating, etc [2–4]. Chemical conversion treatment, for its simple technique with no need for power supply, is commonly used as pretreatment for magnesium alloy, and the typical process mainly adopts chromic anhydride or bichromate as ingredients. To replace the chromate-based chemical conversion treatment on magnesium alloys, much effort was made to develop more benign alternatives [5]. Rare earth based conversion coating applied to aluminum alloy was developed by HINTON [6]. Subsequently it was reported that cerium-based conversion coatings could remarkably

improve the anti-corrosion performance of AZ63, AZ91, AZ31, AZ63 magnesium alloys [7–9], and RUDDA et al [10] successfully prepared rare earth based conversion coatings on pure magnesium, AM60B and WE43 magnesium alloys with Ce, La and Pr nitrates. The rare earth based conversion coatings were believed as a promising alternative to the traditional Cr^{6+} containing process. Although much progress has been made in the processes with cerium salts, currently it is hard to replace the traditional chromate treatment completely for this developing method needs long immersion time or the high treating temperature. It was found that oxidant of H_2O_2 and additive of $\text{Al}(\text{NO}_3)_3$ were helpful in enhancing the coating formation efficiency or improving the coating performance [9, 11], but so far little attention was paid to the other additives and its effect upon the coating growth at low temperature.

In this paper, a $\text{Ce}(\text{SO}_4)_2\text{--H}_2\text{O}_2$ based treating solution is adopted to prepare a chemical conversion coating on AZ91D magnesium alloy. In order to improve the coating formation at room temperature, additives of

$\text{Ni}(\text{NO}_3)_2$ and sodium dodecyl benzene sulfonate are firstly applied to the treating solution, and the effect of different additives on the coating mass gain and anti-corrosion performance is studied. It is found that the additive of sodium dodecyl benzene sulfonate makes a remarkable improvement to the coating formation. SEM, EDS, XRD and GIXD are also adopted to observe the coating morphology and analyze the coating structure and composition. In addition, the potential change curves of the magnesium alloy in the different treating solutions are compared to understand the additives effect on shortening the time needed for the coating growth.

2 Experimental

Firstly, AZ91D magnesium alloy specimens were mechanically polished by grit emery papers. After the pretreatment of degreasing, alkaline deoxidization and acid polishing to remove the surface contamination, the specimens were then treated in chemical conversion bath. The chemical conversion treatment solution was comprised of 5–10 g/L $\text{Ce}(\text{SO}_4)_2$, 5–12 mL/L H_2O_2 . Additives of 3–5 g/L $\text{Ni}(\text{NO}_3)_2$ and 0.1–0.3 g/L sodium dodecyl benzene sulfonate were added to the treating solution, and the effect of additives on the coating performance was studied. All the specimens were treated at room temperature.

Scanning electron microscope (SEM, Feicompany, Quanta 400) with electron beam energy of 25 keV was used to examine the morphology of the conversion coating formed on the magnesium surfaces. Energy dispersive X-ray spectroscopy (EDX, Oxford742d) was used to examine the element composition of the coating. X-ray diffractometer (XRD, D8 Advance, Bruker) was used to study the phase structure of the conversion coatings on the magnesium alloy. In order to study the diffraction from the thin conversion coating and avoid the interference of magnesium matrix, grazing incidence X-ray diffraction (GIXD, D8 Advance, Bruker) technique was applied to determining the coating structure, in which the grazing angle α of the incident beam was set at 1° .

The corrosion resistance of the coating was evaluated by the dropping test with the solution of 5% $\text{PbAc}_2 \cdot 9\text{H}_2\text{O}$. Polarization measurement was also carried out to evaluate the corrosion resistance of the conversion coating. The polarization measurements of the conversion coatings were performed with an electrochemistry station (CS300, China) by linear sweep voltammetry technique at room temperature in 3.5% NaCl solution. The coated specimens were enclosed with epoxy resin so that only 1 cm^2 area was exposed to the electrolyte [12]. The current density (J_{corr}) of corrosion was obtained using corresponding computer software. In

order to understand the influence of additives to the coating formation, the potential change ($\phi-t$ curve) of the magnesium alloy in the treating solution was also recorded with the electrochemistry station. The coating mass gain was calculated by the formula of $m_1 - m_2$, in which m_1 is the mass of the magnesium specimen with the coating, and m_2 is the mass of the magnesium specimen that its coating was dissolved in HNO_3 solution [13].

3 Results and discussion

3.1 Effect of additives in treating solution on coating performance

Figure 1 shows the effect of additives in treating solution on the coating performance. In the treating solution without H_2O_2 , the coating growth is so slowly that a very thin coating can be formed, therefore, it has a low anti-corrosion performance of 20 s in the dropping test solution. Oxidant of H_2O_2 is helpful to the coating growth in the $\text{Ce}(\text{SO}_4)_2$ solution, therefore it can

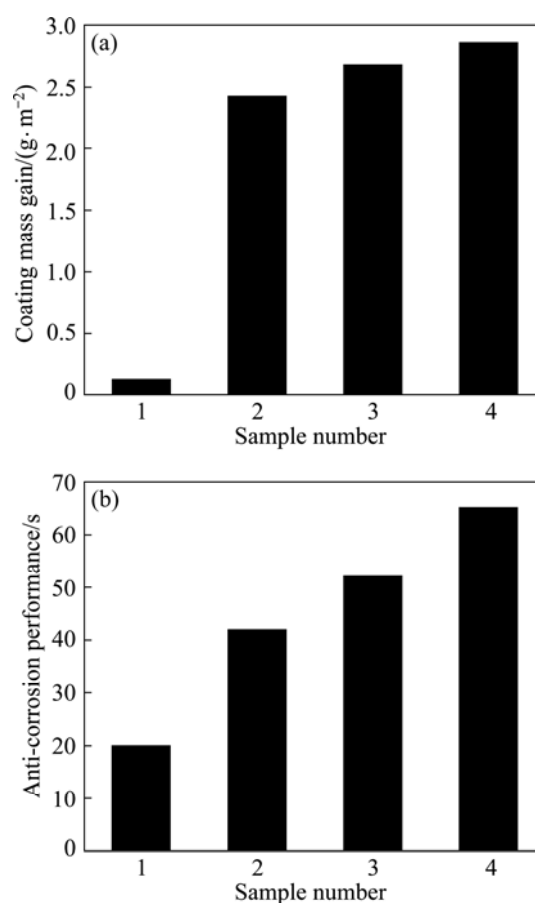


Fig. 1 Effect of additives in treating solution on coating mass gain (a) and anti-corrosion performance (b) (Sample No.1: Treated in $\text{Ce}(\text{SO}_4)_2$ solution; Sample No.2: Treated in $\text{Ce}(\text{SO}_4)_2\text{-H}_2\text{O}_2$ solution; Sample No.3: Treated in $\text{Ce}(\text{SO}_4)_2\text{-H}_2\text{O}_2\text{-Ni}(\text{NO}_3)_2$ solution; Sample No. 4: Treated in $\text{Ce}(\text{SO}_4)_2\text{-H}_2\text{O}_2\text{-sodium-dodecyl benzene sulfonate}$ solution)

drastically enhance the coating mass gain from 0.12 g/m² to 2.417 g/m² and anti-corrosion performance from 20 s to 40 s. When the additives of Ni(NO₃)₂ and sodium dodecyl benzene sulfonate were subsequently added to the treating solution comprised of Ce(SO₄)₂ (10 g/L) and H₂O₂ (12 mL/L), the coating formation is further accelerated, and the coating mass gain increases to 2.679 g/m² and 2.857 g/m², respectively. Sodium dodecyl benzene sulfonate makes more remarkable effect on anti-corrosion performance improvement than Ni(NO₃)₂. The former could improve the anti-corrosion performance from 42 s to 65 s, while the latter could only improve it from 42 s to 52 s.

Potentiodynamic polarization tests were carried out to determine the J_{corr} of different solutions treated specimens, as seen in Fig. 2. The ϕ_{corr} of the specimen treated in Ce(SO₄)₂ solution is -0.394 V, and it will be increased to -0.365 V and -0.325 V, when the additives of Ni(NO₃)₂ and sodium dodecyl benzene sulfonate were applied to the rare earth based treating solution. The J_{corr} values of magnesium alloy matrix and the specimens treated in the solutions of Ce(SO₄)₂, Ce(SO₄)₂-H₂O₂, Ce(SO₄)₂-H₂O₂-Ni(NO₃)₂, Ce(SO₄)₂-H₂O₂-sodium dodecyl benzene sulfonate are 56.2×10^{-5} , 7.41×10^{-5} , 4.05×10^{-5} and 2.20×10^{-5} A/cm², respectively. The coating treated in the sodium dodecyl benzene sulfonate added rare earth solution has the best corrosion resistance, which agrees well with the result of dropping test.

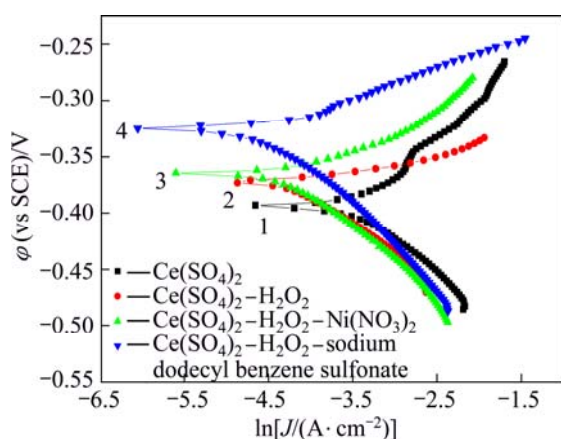


Fig. 2 Polarization curves of magnesium alloy specimens treated in different solutions

3.2 Potential change curves of magnesium alloy in solutions with different additives in the course of coating formation

The coating formation is related to the electrochemical reaction on metal surface, in which the negative potential phase in the substrate acts as an active anode, and the positive potential phase acts as an active cathode in the treating solution [14]. The potential

change of the magnesium alloy specimen in the coating growth process was tracked with an electrochemical measuring system, and the potential change curves were recorded in Fig. 3.

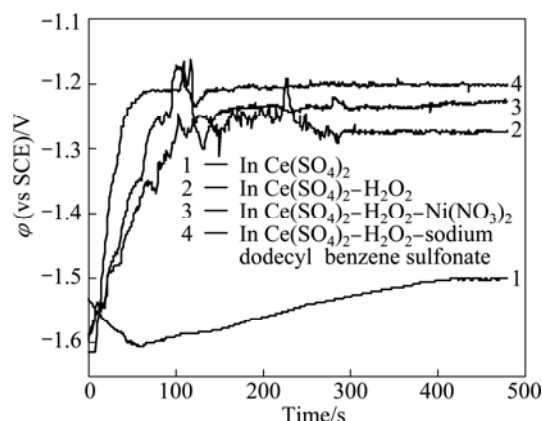


Fig. 3 Potential change of magnesium alloy in different treating solutions

When the specimen was dipped into the solution of Ce(SO₄)₂ without oxidant, the potential moves to negative direction nearly in the first 50 s, and shifts to positive direction when the conversion coating begins to form, but it is hard to reach the stable state. As seen in Fig. 3, oxidant of H₂O₂ could exert a great influence on the potential change curve, which induces the potential move to positive direction quickly and shortens the period to reach the stable state.

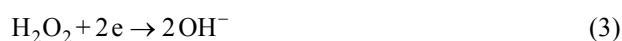
The ϕ - t curve of the coating growth can be divided into three stages. The first stage is the dissolution of Mg alloy:



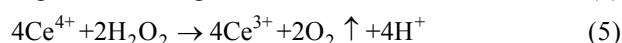
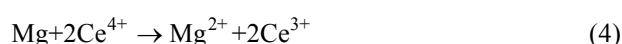
in which the potential quickly increases for the accumulation of the dissolved Mg²⁺ in the interface between Mg matrix and solution, and the negative reaction is described as [15]:



or



In the second stage, the conversion coating begins to grow, and the coating formation equations can be written as [15]:



In this stage, the violent potential vibration is observed, which is caused by the unbalanced coating

dissolution and deposition, and after this period a dense conversion coating has been completely formed so that the potential arrives to the stable state in the third stage.

Figure 3 also shows that all the additives can shorten the time in the second stage, so make a great influence on the shape of $\varphi-t$ curves. Compared to $\text{Ni}(\text{NO}_3)_2$, sodium dodecyl benzene sulfonate is more beneficial to the coating formation for it nearly shortens the second stage of coating formation from 5 min to 2 min. Acting as surfactant, sodium dodecyl benzene sulfonate can improve the deposition of $\text{Ce}(\text{OH})_3/\text{Ce}(\text{OH})_4$ and the growth of the deposited hydroxide particles, so it accelerates the dynamic process of the second stage in the coating formation, which is also supported by the micro-morphology analysis in section 3.3 on the coating formation.

3.3 Micro-morphology of conversion coating

The SEM micro-morphologies of coating are shown in Fig. 4. In the solution of 5 g/L $\text{Ce}(\text{SO}_4)_2$, the formed loose particle-like coating is too coarse to attach on the magnesium matrix, so it has a bad corrosion resistance in the dropping test. Oxidant of H_2O_2 will accelerate the coating growth and improve the coating compactness, thus the anti-corrosion performance is enhanced (see Fig. 1). When additives are added to the treating solution

of $\text{Ce}(\text{SO}_4)_2-\text{H}_2\text{O}_2$, the coating surface appears to be more even than that formed without additives. As seen in Fig. 4(c), the addition of $\text{Ni}(\text{NO}_3)_2$ gives rise to much crack on the coating surface, so it makes little devotion to the corrosion resistance, although it can accelerate the coating growth. A smooth and dense coating with good adhesion can be produced on the magnesium surface when sodium dodecyl benzene sulfonate is added to the bath, and this coating also has the best quality. From the above analysis, it is known that the additive of sodium dodecyl benzene sulfonate is favorable to the oxide deposition in the solution.

3.4 Element composition analysis of conversion coating

EDX was used to analyze the element composition of the coatings formed in different conditions, as shown in Table 1. The samples treated in different solutions have the same element composition, but the additives will change the element content in the coating. The elements of Mg and Al come from the magnesium alloy matrix, and Ce is introduced from treating solution. C element results from the sample preparation for the EDX analysis. The addition of H_2O_2 oxidant to the $\text{Ce}(\text{SO}_4)_2$ solution can accelerate the electrochemistry reaction in the coating formation, so it increases the Ce element

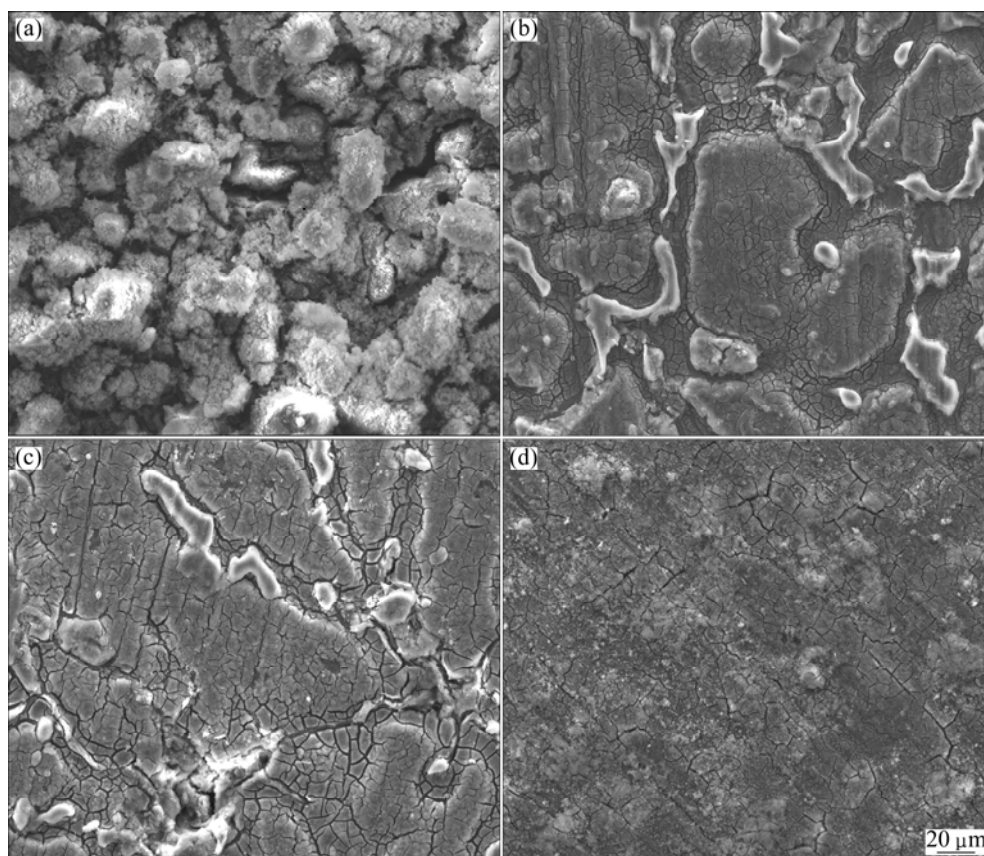


Fig. 4 SEM images of conversion coatings on Mg alloy treated in $\text{Ce}(\text{SO}_4)_2$ (a), $\text{Ce}(\text{SO}_4)_2-\text{H}_2\text{O}_2$ (b), $\text{Ce}(\text{SO}_4)_2-\text{H}_2\text{O}_2-\text{Ni}(\text{NO}_3)_2$ (c), $\text{Ce}(\text{SO}_4)_2-\text{H}_2\text{O}_2$ -sodium dodecyl benzene sulfonate (d) solutions

Table1 Elemental composition of conversion coating treated in different solutions (mass fraction, %)

Solution	w(C)/%	w(O)/%	w(Mg)/%	w(Al)/%	w(Ce)/%	Others
$\text{Ce}(\text{SO}_4)_2$	1.27	36.55	31.14	8.99	15.86	Balance
$\text{Ce}(\text{SO}_4)_2\text{--H}_2\text{O}_2$	6.02	24.23	40.12	7.55	18.92	Balance
$\text{Ce}(\text{SO}_4)_2\text{--H}_2\text{O}_2\text{--Ni}(\text{NO}_3)_2$	4.08	26.71	33.58	6.90	22.32	Balance
$\text{Ce}(\text{SO}_4)_2\text{--H}_2\text{O}_2\text{--sodium dodecyl benzene sulfonate}$	2.73	21.62	44.08	2.41	25.08	Balance

content in the coating from 15.86% (mass fraction) to 18.92%. The additive of sodium dodecyl benzene sulfonate remarkably increases the Ce content in the coating to 25.08%, while $\text{Ni}(\text{NO}_3)_2$ can increase it to 22.32%. Therefore, it is known that all the additives can facilitate the deposition of Ce hydroxides, and sodium dodecyl benzene sulfonate makes the most devotion to the increment of Ce content.

3.5 Micro-structure analysis of conversion coating

Up to now, it is usually believed that conversion coating is mainly composed of CeO_2 or Ce_2O_3 , but few reports refer to the structure of the coating formed in different rare earth treating solutions. In this work, the coating structure was studied to understand the effect of additives on the coating formation. Figure 5(a) shows

the XRD patterns of the coating formed on magnesium alloy in solutions with different additives, which are determined with the $\theta\text{--}2\theta$ X-ray diffraction scan mode. These intense diffraction peaks from 32° to 80° in the XRD patterns are attributed to the two phases of $\alpha\text{-Mg}$ and $\beta\text{-Al}_{12}\text{Mg}_{17}$ in the magnesium alloy, so only the sharp peaks of the bulk material can be recognized from the common XRD analysis. In order to avoid the diffraction peaks influence from the magnesium matrix, grazing incidence X-ray diffraction was used to determine the surface coating, the results are shown in Fig. 5(b). No sharp diffraction peaks were found in these different coatings from the GIXD patterns, so it could be known that all the conversion coatings exhibit amorphous structure and the addition of additives will not lead to the formation of a new structure.

4 Conclusions

1) Oxidant of H_2O_2 is helpful to the coating growth in the $\text{Ce}(\text{SO}_4)_2$ solution, and the additives of $\text{Ni}(\text{NO}_3)_2$ and sodium dodecyl benzene sulfonate in the $\text{Ce}(\text{SO}_4)_2\text{--H}_2\text{O}_2$ treating solution can further improve the coating anti-corrosion performance. Compared to $\text{Ni}(\text{NO}_3)_2$, sodium dodecyl benzene sulfonate makes the more remarkable effect on corrosion-resistance improvement and coating compactness.

2) The additive of sodium dodecyl benzene sulfonate is helpful to the deposition of $\text{Ce}(\text{OH})_3/\text{Ce}(\text{OH})_4$ and the growth of the deposited hydroxide particles, so that it shortens the time of the second stage in the coating formation, and a smooth and compact coating can be formed.

3) The conversion coating is mainly composed of elements of Al, Mg, Ce and O. Additives of H_2O_2 , $\text{Ni}(\text{NO}_3)_2$ and sodium dodecyl benzene sulfonate in the solution all can enhance the Ce content in the formed coating, while the last makes the most remarkable devotion to the increase of Ce content.

4) All the conversion coatings formed in the solutions with different additives exhibit amorphous structure.

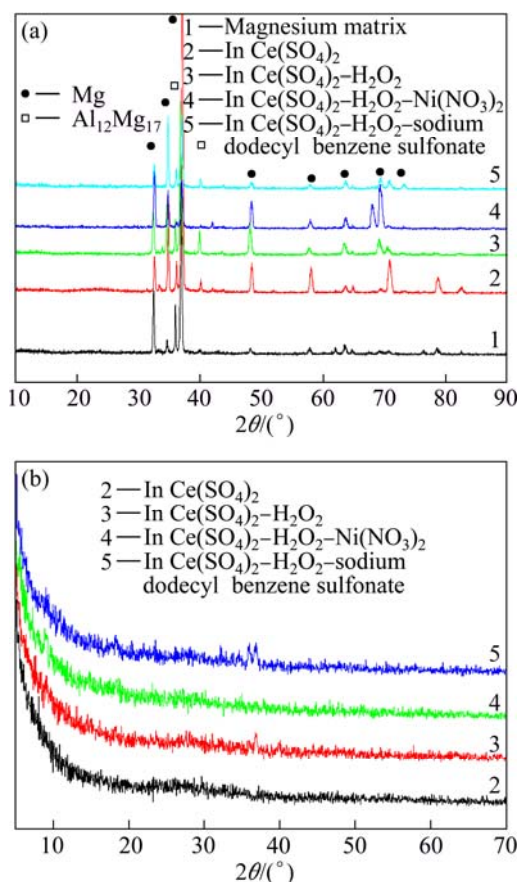


Fig. 5 XRD (a) and GIXD (b) patterns of conversion coating on Mg alloy treated in different solutions

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添加剂作用下制备环境友好型钪基镁合金稀土转化膜

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摘要: 采用 $\text{Ce}(\text{SO}_4)_2\text{-H}_2\text{O}_2$ 溶液体系在 AZ91D 镁合金表面制备环境友好型稀土转化膜, 并在处理液中添加 $\text{Ni}(\text{NO}_3)_2$ 和十二烷基苯磺酸钠以提高室温下的成膜效果。采用 SEM、EDS、XRD、GIXD 等方法研究镁合金表面稀土转化膜的微观形貌与元素组成以及微观结构, 采用自腐蚀电位跟踪法对镁合金在稀土溶液中的成膜过程进行研究。添加剂十二烷基苯磺酸钠比 $\text{Ni}(\text{NO}_3)_2$ 能更有效地提高转化膜的致密性与耐腐蚀性能。与从不含添加剂处理液中得到的转化膜相比较, 添加十二烷基苯磺酸钠得到的转化膜的自腐蚀电流密度从 $7.41 \times 10^{-5} \text{ A/cm}^2$ 降低到 $2.20 \times 10^{-5} \text{ A/cm}^2$, 电位-时间曲线第二阶段的成膜时间从 5 min 缩短到 2 min。稀土转化膜的主要成分为 Mg、Al、O 和 Ce。添加剂 $\text{Ni}(\text{NO}_3)_2$ 和十二烷基苯磺酸钠可分别将转化膜中 Ce 元素的含量从 18.92% 增加到 22.32% 和 25.08%。RXD 与 GIXD 研究表明在所有溶液中得到的转化膜均为非晶态结构。

关键词: 镁合金; 表面处理; 转化膜; 稀土; 添加剂

(Edited by YUAN Sai-qian)