The Composition of the Rare Earth Based Conversion Coating Formed on AZ91D Magnesium Alloy

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As structural materials, magnesium (Mg) alloys have been widely used in the fields of aviation, automobiles, optical instruments, and electronic products. There are few studies on the effect of coating conditions on the compositional variation during the formation process of the conversion coatings. Rare-earth based conversion coating on AZ91 magnesium alloy was prepared in ceric sulfate and hydrogen peroxide contained solution. The element composition and valence as well as their distribution in the coating were analyzed with energy dispersive X-ray spectroscopy (EDS), Electron probe micro-analyzer (EPMA), X-ray photoelectron spectroscopy (XPS). The effect of treating process on the element composition were also studied. It was found that the conversion coating surface consists of Mg, Al, O, Ce, and the weight content of Ce in the coating was affected by the treating solution concentration and immersion time; the Ce element was distributed in the coating non-uniformly and existed in the form of Ce^{+3} and Ce^{+4}, while the O element existed in the form of OH^-, O^{2-}, H_2O. Based on microscopic analysis results, the electrochemical deposition mechanism on the micro-anode and micro-cathode in the process of the coating growth was suggested.

Keywords: magnesium alloy, surface treatment, rare earth, microscopic analysis

1. Introduction

As structural materials, magnesium (Mg) alloys have been widely used in the fields of aviation, automobiles, motorcycles, optical instruments, mechanical equipment and electronic products. However, because the corrosion resistance of Mg alloys is relatively poor, it is necessary to treat their surface to enhance their corrosion resistance. Commonly used surface treatment methods include electroplating, chemical plating, chemical oxidation (conversion), anodic oxidation, micro-arc oxidation and sputtering [1,2]. Chemical oxidation is simple and is often used as the pre-treatment process for Mg alloy coatings to enhance the corrosion resistance of all coatings and the adhesion of organic coatings and substrates. Currently, chromate salts are used as the main component of the coating solution in the chemical oxidation method; however, chromate salts are highly toxic and cause severe environmental contamination. Because of the restricted use of chromium VI (Cr VI) outlined in Chinese and international regulations, such as the "Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment" (RoHS), Cr-free chemical oxidation has become an area of research for Mg alloy surface treatment. Inorganic salts of zirconium (Zr), titanium (Ti), cobalt (Co), molybdenum (Mo) and rare earth elements are primarily used as the main salts for coating solutions in Cr-free chemical oxidation [3-5]. Among these options, rare earth chemical oxidation has attracted much attention because of its appealing characteristics, such as non-toxicity and superior corrosion resistance [6]. Xu [7], Montemor [8], Dabalà [9], Rudd [10] and Yu [11] et al. have prepared rare earth conversion coatings exhibiting good corrosion resistance on the surface of pure Mg and Mg alloys, including AZ91D, AZ31, AZ63, AM60B and WE43, using the nitrate or sulfate salts of the rare earth metals Ce, lanthanum (La) and praseodymium (Pr). Currently, there are a number of studies on coating solution formula development and performance comparison; however, there are few studies on the effect of coating forming conditions on the compositional variation and distribution pattern of the surface elements during the formation process of rare earth conversion coatings on Mg alloys. Therefore, we prepared a rare earth conversion coating on the surface of AZ91D Mg alloy in an orthogonal experiment. Several microscopic analytical methods

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were used to study the elemental composition and distribution of the conversion coating as well as the pattern of influence of the process conditions on the rare earth element content.

2. Experimental Procedure

The AZ91D Mg alloy was used as the substrate. The sample size was 2 cm × 2 cm. The samples were well polished by 250[#], 600[#] and 1200[#] metallographical sand papers. After completion of the pre-treatment procedures, including debinding, etching and activating, the samples were rinsed with water and then dried. Subsequently, a rare earth chemical conversion treatment was performed on the samples. The debinding solution consisted of 5 g·L^{-1} NaOH and 1 g·L^{-1} OP-10; the etching solution consisted of 3 g·L^{-1} oxalic acid; and a 10%-30% NaOH solution was used as the activating solution.

An $L_{16}(3^4)$ orthogonal array was used to design the experimental conditions. The values of the content factor of $Ce(SO_4)_2$ in the treatment solution were 5, 10, 15 and 20 g·L^{-1}; the values of the content factor of H_2O_2 were 4, 8, 12 and 16 mL·L^{-1}; the values of the processing time factor were 2, 4, 6 and 8 min; and all of the temperatures were room temperature. Process optimization was performed according to the 16 experiment groups determined by the $L_{16}(3^4)$ orthogonal array. The evaluation indices for the conversion coatings were corrosion resistance and coating weight. A spot test was used to evaluate the corrosion resistance of the rare earth conversion coatings using 5% aqueous lead acetate ($PbAc_2·9H_2O$) as the spot solution. The time needed for the spot solution on the surface of the conversion coating to change color was used to determine the corrosion resistance of the conversion coating. An analytical balance was used to determine the coating weight using the weighing method.

Backscattered electron images produced by a QUANTA400 scanning electron microscope (SEM) were used to study the phase distributions on the surface of the Mg alloys.

An Oxford742d energy-dispersive X-ray spectrometer (EDX) was used to analyze the chemical compositions of the rare earth conversion coatings. An EPMA1600 electron probe was used to analyze the element area distributions on the surface of the rare earth conversion coatings and the element line distributions on the cross-sections. A Kratos Axis Ultra DLD multifunctional X-ray photoelectron spectroscope (XPS) was used to analyze the valence states of the elements of the rare earth conversion coatings.

3. Resutls and Discussion

3.1 Chemical compositions of the rare earth conversion coatings

There were a total of 16 samples in the orthogonal experiment. Based on the coating formation states and the corrosion resistance performance indices of the conversion coatings, EDX was used to analyze the surface chemical compositions of the rare earth conversion coatings of 8 relatively well formed samples (Table 1). The process details for the samples were as follows: Sample a, 5 g·L^{-1} $Ce(SO_4)_2$ + 4 mL·L^{-1} H_2O_2, 2 min; Sample b, 5 g·L^{-1} $Ce(SO_4)_2$ + 16 mL·L^{-1} H_2O_2, 8 min; Sample c, 10 g·L^{-1} $Ce(SO_4)_2$ + 12 mL·L^{-1} H_2O_2, 8 min; Sample d, 10 g·L^{-1} $Ce(SO_4)_2$ + 16 mL·L^{-1} H_2O_2, 6 min; Sample e, 15 g·L^{-1} $Ce(SO_4)_2$ + 4 mL·L^{-1} H_2O_2, 6 min; Sample f, 15 g·L^{-1} $Ce(SO_4)_2$ + 12 mL·L^{-1} H_2O_2, 2 min; Sample g, 20 g·L^{-1} $Ce(SO_4)_2$ + 12 mL·L^{-1} H_2O_2, 4 min; Sample h, 20 g·L^{-1} $Ce(SO_4)_2$ + 16 mL·L^{-1} H_2O_2, 2 min.

Table 1 shows that the concentration of the main salt for the coating formation, $Ce(SO_4)_2$, was low (5 g L^{-1}). The Ce contents in the rare earth conversion coatings were also relatively low; for instance, the Ce content in Sample a was 4.32%. Increasing the concentration of $Ce(SO_4)_2$ was found to increase the Ce content in the conversion coatings; for example, the Ce content in the conversion coating of Sample e was relatively high (16.53%), with

Table 1 The elemental composition of conversion coatings treated under different process conditions (mass)%

Samples \ Elements	a	b	c	d	e	f	g	h
Mg	74.29	61.14	38.69	52.90	56.51	41.51	37.24	45.47
Al	3.99	3.97	18.14	2.54	3.83	23.11	5.07	13.71
Ce	4.32	10.88	11.52	7.91	16.53	9.99	17.61	5.92
O	17.40	23.59	25.85	32.14	22.81	17.77	22.99	33.97
Other	Remainder	Remainder	Remainder	Remainder	Remainder	Remainder	Remainder	Remainder

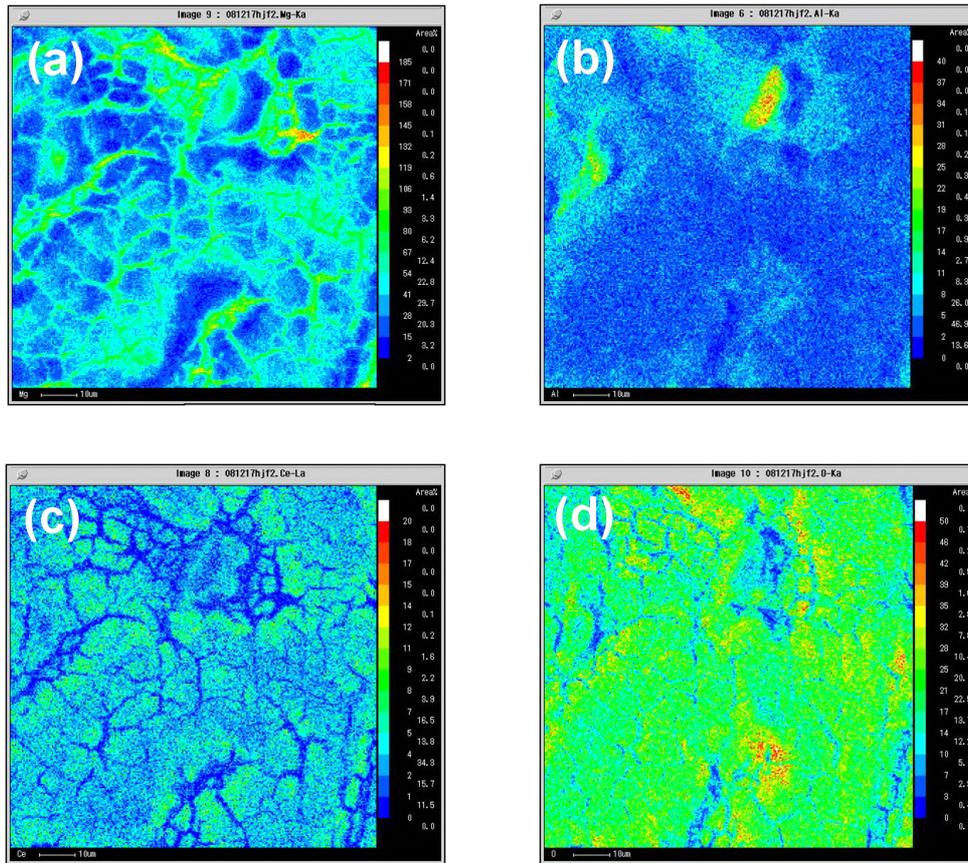**Fig. 1 The elements distribution for (a) Mg, (b) Al, (c) Ce and (d) O in the conversion coating obtained by EPMA.**

a $Ce(SO_4)_2$ concentration of 15 g L^{-1}, and the Ce content in the conversion coating of Sample g reached 17.61% when the $Ce(SO_4)_2$ concentration was increased to 20 g L^{-1}. Increasing the processing time as well as the concentration of the oxidant, H_2O_2, was also found to increase the Ce content in the conversion coating. Despite having the same $Ce(SO_4)_2$ concentration as Sample a, Sample b reached a Ce content of 10.88% by increasing the concentration of H_2O_2 to 16 mL·L^{-1} and increasing the processing time to 8 min. However, the Ce content of Sample h was not significantly increased compared to that of Sample a, likely because of the short coating formation time (2 min). The above analysis showed that increasing the concentrations of the main salt of the treatment solution and the oxidant as well as increasing the processing time leads to an increase in the Ce content in the conversion coating. In addition to the Ce content, the corrosion resistance of the conversion coating is also related to the density of the coating. The influencing factors for the density of a conversion coating are relatively complicated; therefore, a high Ce content does not necessarily result in high corrosion resistance. Please see another study for the optimized

process obtained from the orthogonal experiment based on such evaluation indices as corrosion resistance and coating weight.

3.2 Element distributions of rare earth conversion coatings

3.2.1 Element area distributions on the surface of rare earth conversion coatings

Electron probe microanalysis (EPMA) was used to study the element distributions on the surface of the rare earth conversion coatings on the Mg alloy (Fig. 1). Because of the uneven distribution of the micro-cathode phase on the surface of the Mg alloy, the concentrations of Ce and Al deposited in the cathode phase were inconsistent (Figs 1b , c). Fig. 1c also shows that the distribution of Ce exhibited a block pattern with a relatively low Ce content between the blocks, which may be a result of an uneven deposition reaction occurring at the micro-cathode during the coating formation process. Because of the uneven distribution of metal elements, the concentration of O was also inconsistent on the surface of the conversion coating (Fig. 1d).
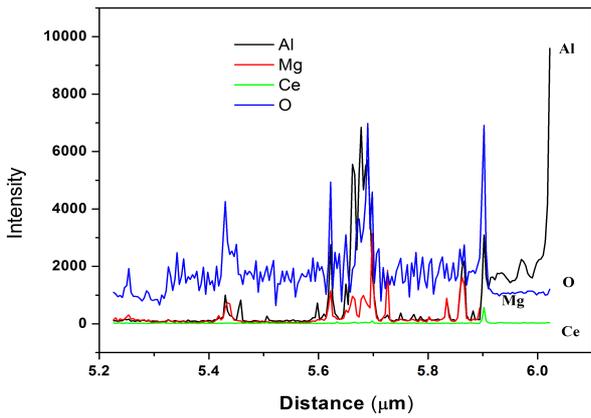
Fig. 2 The elements distribution in the cross-section of the conversion coating on Mg alloy detected by EPMA.

3.2.2 Element line distributions on cross-sections of rare earth conversion coatings

Fig. 2 shows the scanning image of the elemental line distributions on the cross-sections of the Mg alloy rare earth conversion coatings. Along the cross-section, the distributions of Mg, Al, Ce and O were essentially even

within the range of 5.2 m to 6.0 m (the density of the conversion coating was less than 1 μm). However, because the deposition of oxides occurred at the micro-cathode [12], the potential presence of nucleation depositions of oxides at the micro-cathode may lead to a sharp increase in the local concentration.

3.3 XPS analysis of rare earth conversion coatings

XPS was also used to study the rare earth conversion coatings on the Mg alloy. Figs 3a, b and c show the spectra of all the elements, O and Ce, respectively. Fig. 3a shows that the conversion coatings consist mainly of Mg, Al, Ce and O, which is in agreement with the EDX analysis. In addition, carbon (C) was observed to have originated from the sample preparation, whereas iron (Fe) and calcium (Ca) likely originated from the substrate. There were two peaks observed in the spectrum of O. Peak-peak fitting could be performed by combining the O^{2-} in the oxides, OH^- in the hydroxides and O from H_2O in the hydrates. It was discovered from this fitting that O existed in the forms of O^{2-}, OH^- and H_2O; i.e., the deposits in the conversion coatings could be a mixture of oxides, hydroxides and hydrates. Lastly, two peaks were observed
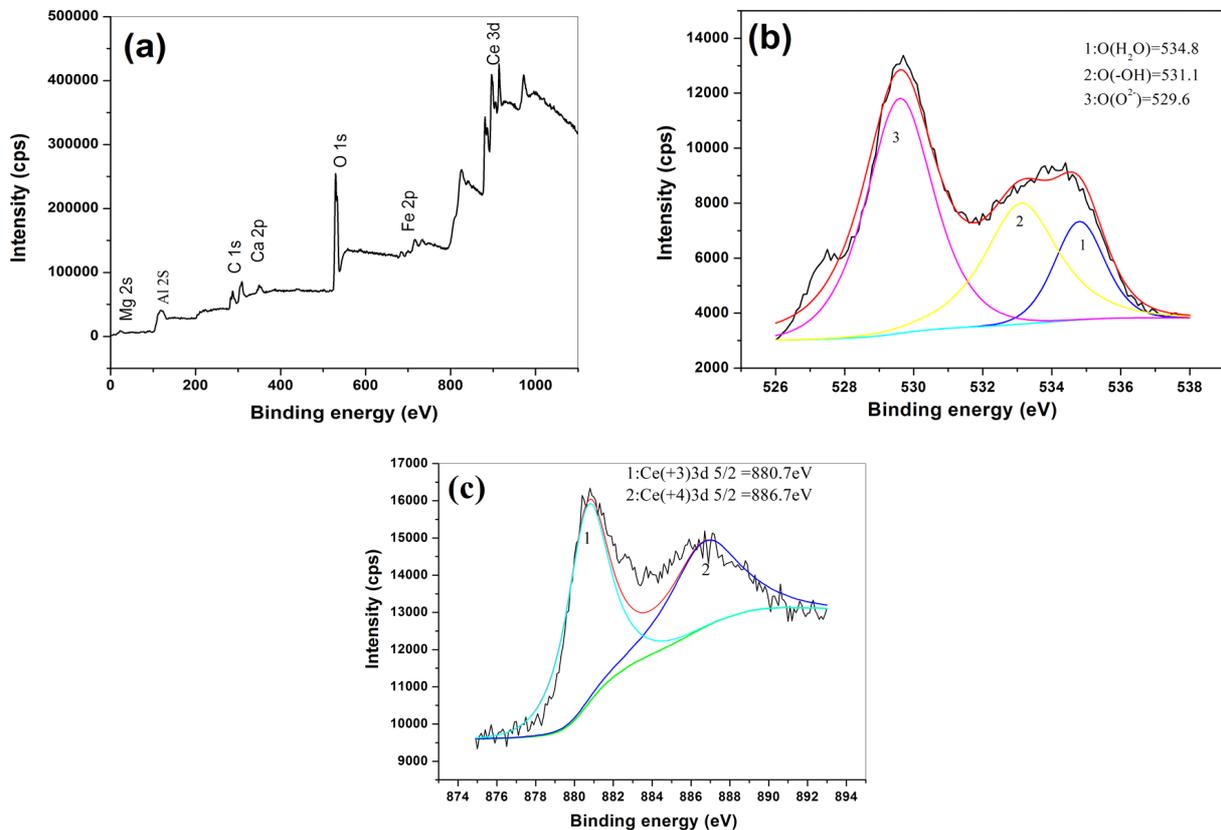

Fig. 3 XPS spectra of the conversion coating, (a) full range surveyed spectra; (b) oxygen 1s spectra; (c) Ce Cerium 3d spectra.

in the spectrum of Ce, for which a fitting could be performed by combining Ce^{+3} and Ce^{+4}. It was discovered from this fitting that Ce existed in two valence states, i.e., Ce^{+3} and Ce^{+4}, from the corresponding oxides Ce_2O_3 and CeO_2 or the corresponding hydroxides $Ce(OH)_3$ and $Ce(OH)_4$, respectively.

4. Conclusions

(1) Rare earth conversion coatings were prepared on the surface of a Mg alloy using the ceric sulfate and hydrogen peroxide aqueous solution method. The major compositional elements of the rare earth conversion coatings were Mg, Al, O and Ce. Increasing the concentrations of ceric sulfate or hydrogen peroxide in the treatment solution or increasing the processing time subsequently led to an increase in the Ce content in the conversion coatings.

(2) The area distributions of Ma, Al, O and Ce in the rare earth conversion coatings were uneven. Ce selectively deposited at the micro-cathode, and its distribution exhibited a block shape. The elemental line distributions on the cross-sections of the conversion coatings were essentially even; however, because of the emergence of oxide nucleation depostions, the concentration sharply increased on the cross-sections.

(3) The O in the conversion coatings existed in the forms of O^{2-}, OH^- and H_2O, and Ce existed in the forms of Ce^{+3} and Ce^{+4}. The deposits in the conversion coatings could be a mixture of oxides, hydroxides and hydrates.

References

1. R. Fu, *Automob. Technol. Mater.*, **7**, 71 (2004).
2. B. Li and Z. Shen, *J. Mater. Protect.*, **35,** 1 (2002).
3. J. Wang and Y. Ding, *J. Mater. Protect.*, **39**, 38 (2006).
4. H. Umehara, M. Takaya, and S. Terauchi, *Surf. Coat. Technol.*, **169-170**, 666 (2003).
5. J. Qian, D. Li, and B. Guo, *J. Mater. Protect.*, **35**, 5 (2002).
6. L. Li, J. Lei, S. Zhang, D. Li, and Y.-J. Tian, *J. Mater. Eng.*, **10**, 60 (2006).
7. Y. Xu, X. Chen, Z.-S. Lu, and Y.-J. Li, *J. Chin. Rare Ear. Soc.*, **23**, 40 (2005).
8. M. F. Montemor, A. M. Simöes, and M. J. Carmezim, *Appl. Surf. Sci.*, **253**, 6922 (2007).
9. M. Dabalá, K. Brunell, E. Napolitani, and M. Magrini, *Surf. Coat. Technol.*, **172**, 227 (2003).
10. A. L. Rudd, C. B. Breslin, and F. Mansfeld, *Corros. Sci.*, **42,** 275 (2000).
11. S. X. Yu, Q. Y. Lu, J. HAN, Z,-W. Zhang, and Q.-Y. Zhang, *J. Rare Earth.*, **24**, 397 (2006).
12. D. André and J. P. Petitjean, *J. Surf. Coat. Technol.*, **194**, 1 (2005).