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IMPROVEMENT OF CORROSION RESISTANCE OF AZ91D MAGNESIUM ALLOY BY LANTHANUM-BASED CONVERSION COATING

RINGKASAN: *Salut tukaran kimia dengan larutan garam logam nadir bumi dianggap sebagai satu alternatif kepada salut tukaran kromat untuk memperbaiki rintangan karatan aloi-aloi magnesium. Dalam kajian ini, salut tukaran dengan lanthanum dibentuk ke atas aloi magnesium AZ91D telah dicirikan dan kesan perawatan masa dibincangkan. Imej-imej "Scanning Electron Microscope" (SEM) menunjukkan spesimen yang dirawat dengan larutan lanthanum nitrat dan magnesium nitrat selama 30 minit telah membentuk satu lapisan oksida keseluruh permukaan aloi magnesium tersebut. Analisis EDS telah membuktikan bahawa lapisan tersebut terutamanya terdiri daripada unsur oksigen dan lanthanum. Ujian karatan menunjukkan salut tukaran dengan lanthanum mempunyai rintangan karatan yang lebih baik berbanding spesimen tanpa rawatan pada semua keadaan rawatan.*

ABSTRACT: Chemical conversion coating by rare earth metal salt solution was considered as an alternative to chromate conversion coating in order to improve the corrosion resistance of magnesium alloys. In this study, lanthanum-based conversion coatings formed on AZ91D magnesium alloy were characterized, and the effect of treatment period was discussed. SEM images showed that specimen treated with solution containing lanthanum nitrate and magnesium nitrate for 30 min has formed an oxide layer on the entire surface of magnesium alloy. EDS analysis has confirmed that the layer was mainly consisted of oxygen and lanthanum elements. Corrosion test indicated that lanthanum-based conversion coating has a better corrosion resistance than as-received specimen at all treatment conditions.

Keywords: Corrosion protection, magnesium alloy, conversion coating, rare earth element (REE)

INTRODUCTION

Magnesium is widely distributed in the earth; it is the eighth elements in order of both terrestrial and cosmic abundance (Emley, 1966). Magnesium alloy has been used widely in electronics, electrical devices and automotive industries because of its superior properties such as low density, outstanding strength to weight ratio, excellent dimensional stability, and good machinability (Song *et al.*, 1999). However, their corrosion protections are limited because of their high chemical reactivity. Therefore it is necessary to do surface treatment properly onto the surface of the magnesium alloy to improve the corrosion resistance (Gray *et al.*, 2002).

Many surface treatment techniques have been proposed and mainly treatments include conversion coating, electro-plating/electroless and anodic coating (Yamamoto *et al.*, 2001). Conversion coatings are produced by chemical or electrochemical treatment of a metal surface to produce a superficial layer of substrate metal oxides, chromates, phosphates, or other compounds that are chemically bonded to the surface (Lowenheim, 1974). Different types of conversion coating include chromate, phosphate/permanganate and fluorozirconate treatments (Gray *et al.*, 2002). Conversion coating is one of the most cost effective and simplest processes for introducing a metallic coating to a magnesium substrate (Delong *et al.*, 1984).

Chemical conversion treatment is an easy method to grow a good corrosion resistance film on the surface of the magnesium alloy. Such film can also improve the adhesion ability between the coating and the substrate which makes it easy for the next process. The most widely used is chromate solution, DOW7, which is produced by Dow Chemical Company in Japan. The film has excellent corrosion resistance and adhesion ability (Ono *et al.*, 2001). However the disadvantage of this treatment process is the environment pollution due to the waste water containing hexavalent chromate (Cr_6^+) and the health-related concerns with people (Umehara *et al.*, 2001). Now, the great need is to develop new chrome-free chemical treatment methods to replace the current method. The phosphate, phosphate/permanganate (Kim *et al.*, 2004), and stannate-based (Gonzalez-Nunez *et al.*, 1999) processes are investigated. Some researchers reported that the corrosion resistance of magnesium was improved by the formation of a surface oxide film containing rare earth elements (REE) (Brunelli *et al.*, 2005).

In this paper, we produced an oxide film containing La on AZ91D magnesium alloy by conversion coating in nitrate solution, whereby the effect on the corrosion resistance against salt water was investigated. The influence of coating time period is also discussed.

MATERIALS AND METHODS

The commercial AZ91D magnesium alloy was employed as specimen. Its chemical composition is given in Table 1. The specimens were embedded in resin form except for one surface (about 10 mm^2) in order to control the active area. The sample's surface without resin was polished with emery papers of grit #1000 to ensure that the same surface roughness is obtained for different tested specimens.

All conversion coating experiments were performed in solution containing 0.1 mM $La(NO_3)_3$, 0.1mM $Mg(NO_3)_2$ and 0.1 mM $La(NO_3)_3$ + 0.1mM $Mg(NO_3)_2$. The specimen was immersed at room temperature with different period of time treatment ranging from 10 - 60 min. After the treatment process, the specimens were thoroughly rinsed with distilled water and then air dried for 24 hours at 343 K in order to get them denitrated.

The anti-corrosive properties of the anodic films were examined against salt water. The corrosion rate of the specimen was measured in accordance with JIS H 0541(Japanese Standards Association, 2003). The specimen was immersed for 72 hours in NaCl solution of 0.5 dm^3. The NaCl concentration was 50g/dm^3, and the pH was adjusted at 10 - 11 by $Mg(OH)_2$. The specimen was rinsed with distilled water, where the corrosion product formed on the surface was removed with a plastic brush. The weight of specimen was measured, whereby the corrosion rate, R (mm/year) was calculated using the following equation;

$$R = \frac{8.76 \times 10^4 W}{ADt} \qquad (1)$$

Where W, A, D and t are weight change (g), active area (cm^2), density (g/cm^3) and immersion time (h), respectively.

The microstructure and surface morphology of the specimen was observed by Optical Microscope (OM) and Scanning Electron Microscope (SEM), coupled with Energy Dispersive Spectroscopy (EDS).

Table 1. Chemical analysis of AZ91D (wt. %).

Alloy	Al	Mn	Zn	Si	Cu	Ni	Fe	Other	Mg
AZ91D	8.5 - 9.5	0.17 - 0.4	0.45 - 0.9	<0.05	<0.008	<0.001	<0.004	<0.001	Bal.

RESULTS AND DISCUSSION

Surface analysis

A thin coating layer was formed on the specimen by the conversion coating. Figure 1 shows the surface morphologies of the (a) untreated specimen and (b) specimen immersed in 0.1mM $La(NO_3)_3$ + Mg $(NO_3)_2$ solutions for 30 min. The lanthanum and magnesium treated specimens have shown a network resembling a micro-cracked surface coating. These cracks may be attributed to hydrogen being released through a chemical reaction process during the coating formation period. The tendency for the self-healing action increases with increasing lanthanum ion concentration. This could be explained by the increase of the coating thickness as shown in Figure 1(b). Mg, O and La elements were detected by EDS, both on the crevices and the oxide film as shown in Table 2(a). On the other hand, the polishing flaw could also be seen on the surface of the untreated specimen as shown in Figure 1(a); however O and La elements were not detected for the untreated specimen as shown in Table 2(b).

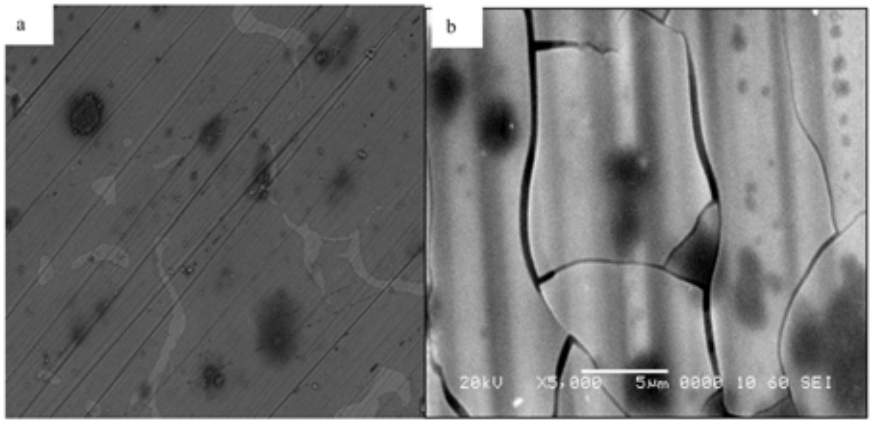

Figure 1: *SEM images of (a) untreated and (b) specimen treated with $La(NO_3)_3$+$Mg(NO_3)_2$ electrolytes for 30 min.*

Table 2. EDS analysis of a) untreated and b) specimen treated with $La(NO_3)_3$+$Mg(NO_3)_2$ solution for 30 min

(a)

Composition	O	Mg	Al	La
Mass (%)	0	74.97	25.03	0

(b)

Composition	O	Mg	Al	La
Mass (%)	38.42	35.93	16.47	0.71

Corrosion Behavior

The corrosion rate of the specimen with conversion coating by immersion in the $La(NO_3)_3$ solutions at different immersion time period is shown in Figure 2. The untreated specimen has shown the highest corrosion rate of 13 mm/year, compared to the corrosion rate of conversion coated specimen. The result indicated that the conversion coating formed on the surface of AZ91D alloy provides the best corrosion resistance when immersed in $La(NO_3)_3$ solution for 50 min.

Figure 3 shows the corrosion rates of specimen with conversion coating by immersion in $Mg(NO_3)_2$ solutions at different immersion time periods. It can be seen that the corrosion rate of the specimens treated with $Mg(NO_3)_2$ solution have given a good corrosion resistivity compared to the specimen without coating; whilst the specimen which was immersed in $Mg(NO_3)_2$ solutions for 40 min has shown slightly better corrosion resistance than others. It was reported that the corrosion resistance of magnesium metal was considerably better by these treatments (Brunelli et al., 2005), but only few works are reported for magnesium alloys in this study. Since the corrosion resistance of magnesium alloys are much better than magnesium metal, the conversion coating by immersion in electrolyte including either $La(NO_3)_3$ or $Mg(NO_3)_2$ is not good enough for the improvement of the corrosion resistance of magnesium alloy.

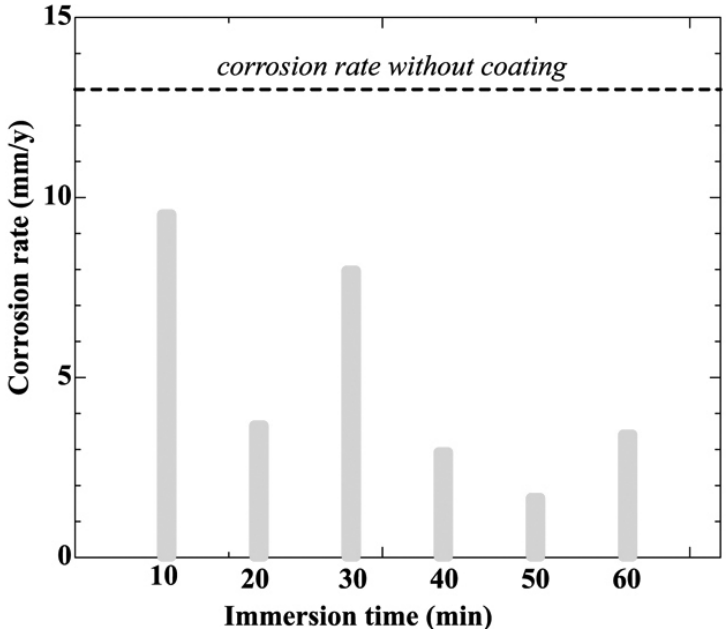

Figure 2. *Corrosion rate of specimen with conversion coating by immersion in La $(NO_3)_3$ electrolyte at different immersion time period.*

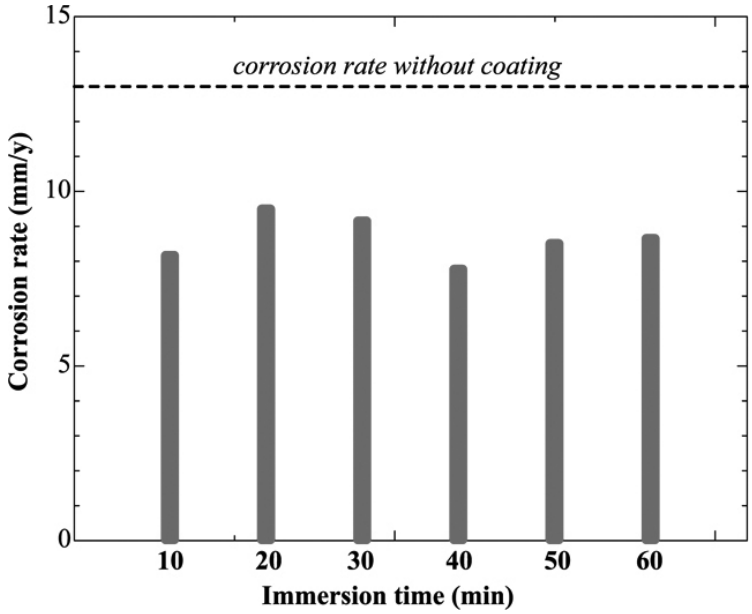

Figure 3. *Corrosion rate of specimen with conversion coating by immersion in Mg $(NO_3)_2$ electrolyte at different immersion time period.*

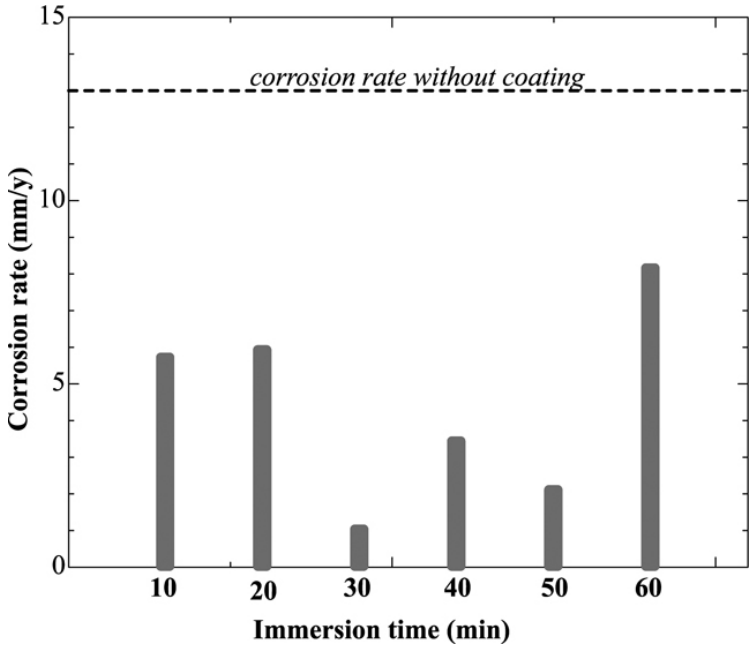

Figure 4. *Corrosion rate of specimen with conversion coating by immersion in $La(NO_3)_3$ and $Mg(NO_3)_2$ electrolytes at different immersion time period.*

The corrosion resistance of AZ91D magnesium alloy was remarkably improved by conversion coating in both $La(NO_3)_3$ and $Mg(NO_3)_2$ electrolytes as shown in Figure 4. The results demonstrated that the specimen treated with conversion coating by immersion in $La(NO_3)_3 + Mg(NO_3)_2$ electrolytes for 30 min has given the highest corrosion resistance of 1.03 mm/year. From our previous work (Toshihide Takenaka *et al.*, 2008), the corrosion resistance of the chromate-based AZ91D magnesium alloy was approximately 2.4 mm/year. Therefore, our presented conversion coating has a potential to replace the chrome-based conversion coating treatment.

The captured SEM images also revealed that the conversion coating with both $La(NO_3)_3$ and $Mg(NO_3)_2$ for 30 min gave pitting free surface after being immersed in the NaCl for 72 hours as shown in Figure 5. This coating was found to be more compact with obviously less in the number of cracks and pores (Figure 5b). In contrast, large pores and cracks clearly appeared on the untreated specimen due to the pitting corrosion (Figure 5a).

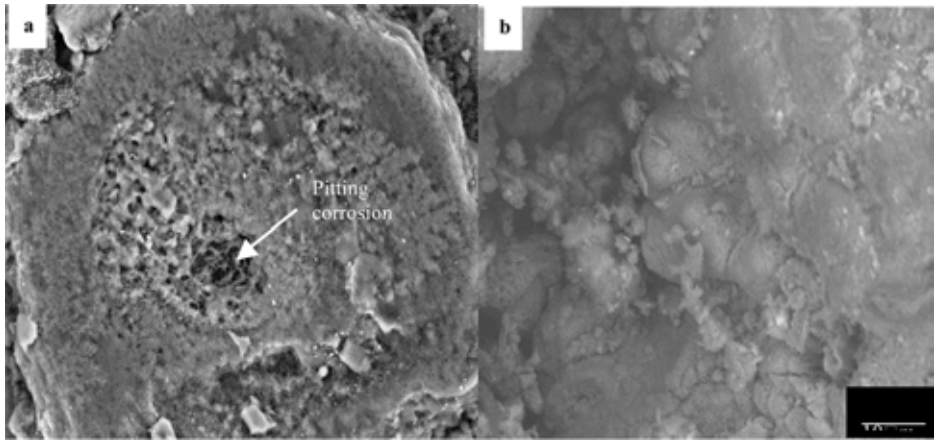

Figure 5. *SEM images of a) untreated, and b) specimen immersed in $La(NO_3)_3 + Mg(NO_3)_2$ electrolytes for 30 min.*

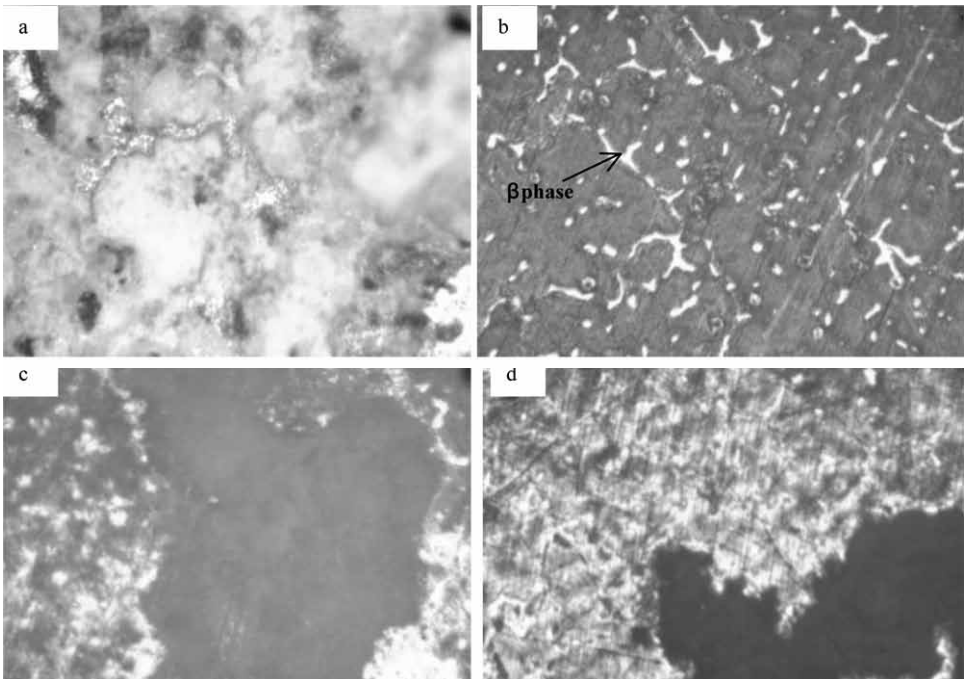

Figure 6. *Optical micrograph images of specimens (a) untreated, (b) $La(NO_3)_3 + Mg(NO_3)_2$ (c) $La(NO_3)_3$ and (d) $Mg(NO_3)_2$ solutions after immersion in NaCl solution for 72 hours.*

Figure 6 shows the optical micrographs of (a) untreated specimen, (b) $La(NO_3)_3$ + $Mg(NO_3)_2$ (c) $La(NO_3)_3$ and (d) $Mg(NO_3)_2$ solutions after immersion in NaCl solution for 72 hours. It can be observed that the surface of lanthanum-treated specimen is more homogeneous with β phase distributed throughout the whole surface (Figure 6b). This indicated that, the combination of $La(NO_3)_3$ electrolyte and Mg $(NO_3)_2$ electrolyte could improve the corrosion resistance of AZ91D magnesium alloy significantly. However, the corrosion resistances of other specimens were inferior throughout the whole surface.

CONCLUSION

A new chemical conversion coating was produced on AZ91D magnesium alloy by immersion in aqueous solutions containing $La(NO_3)_3$ and $Mg(NO_3)_2$ at ambient temperature for 10-60 min at constant concentration of aqueous solutions. SEM and EDS analyses showed that the lanthanum-based conversion coating exhibited chemical compositions that were uniform and the coating was enriched with La with some closed microcracks. The corrosion resistance of AZ91D magnesium alloy was significantly improved by the conversion coating in the solution containing both $La(NO_3)_3$ and $Mg(NO_3)_2$, especially for specimens immersed in 0.1mM $La(NO_3)_3$ + 0.1mM $Mg(NO_3)_2$ solutions for 30 minutes. The finding provides an interesting alternative to the undesirable Cr_6^+based coatings for magnesium alloys.

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