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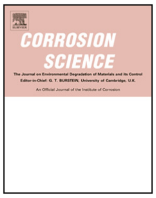

Corrosion resistance of plasma electrolytic oxidation layer of a non-ignitable Mg–Al–Mn–Ca magnesium alloy

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ABSTRACT

A non-ignitable Mg-Al-Mn-Ca magnesium alloy denoted as AMX602 was treated by plasma electrolytic oxidation (PEO) in phosphate - silicate mixture electrolyte, and the morphology, compositions and corrosion resistance of PEO layer on AMX602 alloy were investigated and compared to those of PEO layer on AZ31B alloy. The influence of intermetallic compounds on corrosion resistance of PEO layer on AMX602 alloy was discussed. The results suggest that the chemical composition and structure of PEO layer are influenced by the intermetallic particles in AMX602 alloy, and the corrosion resistance of PEO layer on AMX602 alloy is inferior to that on AZ31B alloy.

1. Introduction

Magnesium is the lightest metal among practical metals, and the weight density of 1740 kg m^{-3} is only about 2/3 of that of aluminum that is widely used as light-weight metals. Magnesium alloys are expected as light-weight materials that will improve fuel efficiency of automobiles, portability of handheld tools and responsibility of mechanical parts. However the application of magnesium alloys is restricted within narrow limits because of their ignitability and poor corrosion resistance [1,2].

The ignitability is a disadvantage of Mg and its alloys, especially when they are in the process of melting and casting. This burdensome property can be explained by Pilling–Bedworth ratio, i.e. the ratio of molar volume of the elementary unit cell of a metal oxides to that of the corresponding metal [3]. Since the Pilling–Bedworth ratio of magnesium is less than 1, oxide products can not cover completely the surface, so that oxidation reaction takes place easily. Therefore, Mg and ordinary Mg alloys always ignite before being melted down in the air. Addition of Ca to Mg alloys has been found to be able to suppress the ignition of Mg alloys [4–6]. The ignition-protective layer formed on the surface of Mg alloys modified by addition of Ca consists of an outer layer of CaO with thickness of 6–20 nm and an inner layer of MgO–CaO mixture [5]. Non-ignitable AMX602 alloy was developed by adding about 2 wt% Ca to AM60 Mg alloy.

In order to improve the corrosion resistance of Mg alloys, on the other hand, various coating technologies have been developed [7]. Plasma Electrolytic Oxidation (PEO), also called as Micro Arc Oxidation (MAO), is one potential coating technology for the improvement of corrosion resistance of magnesium alloys [8–10]. In PEO process, a high anodic voltage not less than 200 V is applied to the Mg alloy substrate, and visible plasma or micro arc is generated on the surface of Mg alloys. In this process, the surface of Mg alloys is locally melted and glassy or ceramic coatings are formed on the surface [10]. Alkaline solutions containing aluminate [11–14], silicate [15–21] or phosphate [22–28] are often used as electrolytes for PEO of magnesium alloys. Our previous work shows that a mixture electrolyte of phosphate and silicate is more favorable for improving the corrosion resistance of PEO layers of Mg alloys than the single electrolyte of phosphate or silicate [29].

Although some studies have been reported with regard to corrosion behavior of non-ignitable Mg alloys [30–33], there is few study about corrosion resistance of coatings on non-ignitable Mg alloys [34], and corrosion resistance of PEO layer formed on AMX602 alloy has not been reported. In the present study, AMX602 alloy was treated by PEO in a mixture alkaline electrolyte of phosphate and silicate, and the corrosion resistance of PEO layer on AMX602 alloy was investigated and compared to that of PEO layer on common AZ31B alloy.

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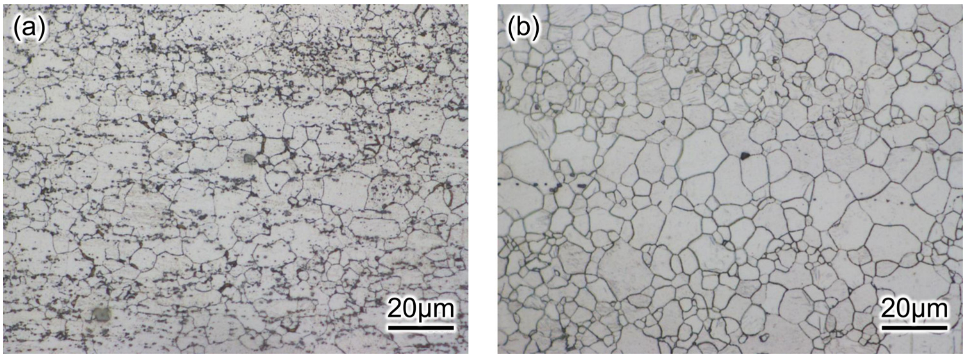

Fig. 1. Microstructures of Mg alloys: (a) AMX602 alloy, (b) AZ31B alloy.

Table 1
Chemical compositions of AMX602 and AZ31B alloys (wt.%).

wt%							
Alloy	Al	Zn	Mn	Si	Fe	Ca	Mg
AZ31B	3.34	1.13	0.350	0.020	0.002	–	Balance
AMX602	6.16	<0.01	0.228	0.003	0.006	2.02	Balance

2. Experimental

Extruded AMX602 and AZ31B alloy plates with width of 75 mm and thickness of 4 mm were cut into specimens with dimensions of 75 × 130 × 4 mm. The chemical compositions of the two Mg alloys are given in Table 1. Before PEO treatment, the specimens were degreased by ultrasonic cleaning in acetone. Both front surface and back surface with total area of 130 cm^2 of the specimen were exposed in electrolyte solution for PEO, and the remaining region was coated with masking tape.

The electrolyte for PEO treatment was prepared by using tri-sodium phosphate (Na_3PO_4) and sodium metasilicate 9-hydrate ($Na_2SiO_3{\cdot}9H_2O$), and the concentration of Na_3PO_4 and $Na_2SiO_3{\cdot}9H_2O$ was 1.37 g dm^{-3} and 24 g dm^{-3}, respectively. KOH was used to adjust the pH value of the electrolyte to be 13.5, and the conductivity of the final electrolyte was 53.3 S m^{-1}. The PEO was carried out using a pulsed power supply, and the on-pulse time was 1 ms while the on–off pulse time ratio t_{on}: t_{off} was 1:5. The coatings were obtained at a constant current density of 200 A m^{-2} until the voltage up to 350 V and then at a constant voltage of 350 V. The details of PEO treatment are described elsewhere [29]. For convenience in comparing the corrosion resistance of PEO layers on AMX602 and AZ31B alloys, PEO treatment time was designed to be 10 and 12 min for AMX602 and AZ31B alloys, respectively, so that the thickness of PEO layers on AMX602 and AZ31B alloys was at the same level (i.e. about 10 μm). After PEO treatment, all specimens were rinsed with distilled water and dried in air immediately.

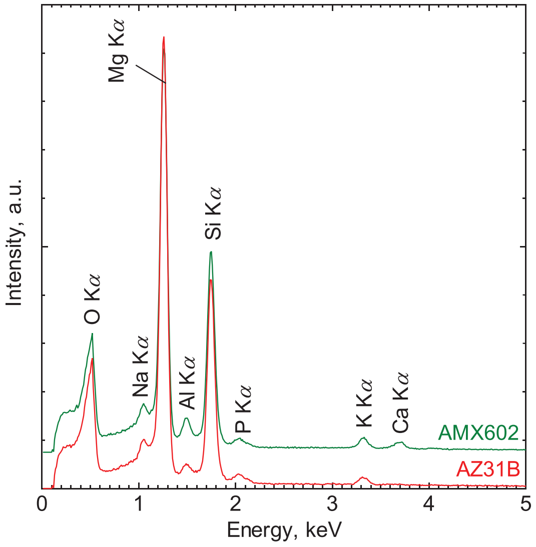

Fig. 3. EDS spectra of PEO layers formed on AMX602 and AZ31B alloys.

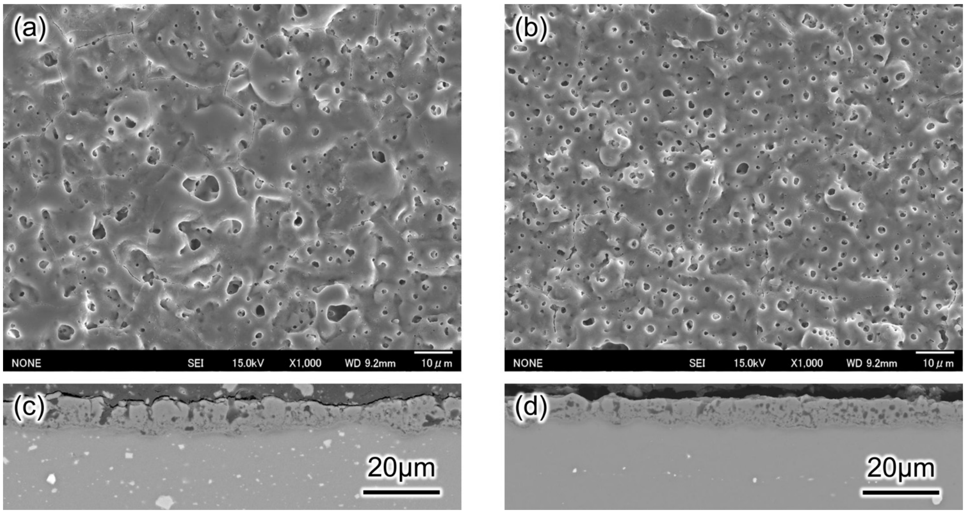

Fig. 2. SEM images of surface and cross-section of PEO layers formed on AMX602 alloy (a, c) and AZ31B alloy (b, d), showing more porous structure of PEO layer on AMX602 alloy than AZ31B alloy.