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Surface modification of ACM522 magnesium alloy by plasma electrolytic oxidation in phosphate electrolyte

Shunsuke Yagi [a,*], Akihiro Sengoku [b], Kohei Kubota [c], Eiichiro Matsubara [b]

[a] Nanoscience and Nanotechnology Research Center, Osaka Prefecture University, Osaka 599-8570, Japan
[b] Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan
[c] Alconix Diecast Suzhou Co., Ltd., Jiangsu 215164, China

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ABSTRACT

Plasma electrolytic oxidation (PEO) on a newly designed ACM522 magnesium die-casting alloy has been conducted in an aqueous phosphate solution and the morphology and corrosion resistance of the PEO films were investigated in detail. By covering the whole surface of the substrate with the PEO film, the corrosion resistance was significantly improved; the modified surface endured a salt spray test for 168 h. It was also clarified that traces of local breakdown caused by excessive PEO can be a cause of pitting corrosion, resulting in significant decline in corrosion resistance with PEO time.

1. Introduction

Magnesium alloys exhibit many superb properties, such as low cutting resistance, high dimensional stability, high dent resistance, high attenuation characteristics, electromagnetic shielding. Furthermore, magnesium has a high specific strength; the density of magnesium is only 2/3 that of aluminum and 1/4 that of iron [1]. Therefore, magnesium alloys are expected to be useful as structural materials in the automotive and aerospace fields, but their high susceptibility to corrosion impedes such applications. The surface of magnesium is easily oxidized to dissolve in solution or to form an oxide or hydroxide layer [2]. Moreover, the resulting magnesium oxide layer does not completely cover the whole surface of the underlying metallic magnesium or magnesium alloy because the formation of magnesium oxide results in a volume decrease of about 20% relative to the volume of the metallic magnesium. This prevents magnesium from forming a robust passivation (oxide) film on its surface as occurs for other less noble metals, such as aluminum. Because of this, many studies on plasma electrolytic oxidation (PEO, also called plasma anodizing or micro-arc oxidation) have been reported to improve the corrosion resistance of magnesium alloys [3–17]. For example, Ghasemi et al. reported PEO of AM50 magnesium alloy using a phosphate bath, and evaluated its final corrosion resistance by electrochemical impedance spectroscopy [4]. Murakami et al. also reported corrosion resistance properties of PEO-treated high-purity cast magnesium and magnesium alloys (AZ31B, AZ91D) with a practical salt spray test after making a scratch on the surface [6].

Recently, ACM522 magnesium die-casting alloy has been designed as a lightweight heat-resistant alloy with high mechanical strength and creep resistance at high temperatures for automobile engine blocks, body panels, and wheels. ACM522 was named after its composition of about 5 wt.% aluminum, 2 wt.% calcium, and 2 wt.% misch metal. It is a zinc-free magnesium alloy, and thus the texture of ACM522 is different to those of AZ91 and AZ31. For example, calcium and aluminum are segregated around the crystal grains of magnesium in ACM522, and it is unclear whether PEO will also be an effective way of corrosion proofing of ACM522. Therefore in the present work, we demonstrated PEO on ACM522 using a simple alkaline phosphate solution; the use of such a simple solution clearly brings out the effects of the phosphate addition. Furthermore, the morphology, composition, and structure of PEO films formed on ACM522 were studied, and the corrosion resistance properties were investigated in detail both by electrochemical methods and a practical salt spray test. To the best of the authors' knowledge, this is the first paper reporting PEO for corrosion-proofing of ACM522 magnesium alloy.

2. Experimental

The composition of the ACM522 magnesium alloy employed in this work is shown in Table 1. For the PEO treatment, ACM522 magnesium alloy 7 cm^2 in surface area was used as the working

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[*] Corresponding author.
E-mail address: s-yagi@21c.osakafu-u.ac.jp (S. Yagi).

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Table 1
Composition of ACM522 magnesium alloy.

	Mg	Al	Misch metal (mainly Ce and La)	Ca	Mn	Fe	Cu	Ni
wt.%	Balance	5.3	2.6	2.0	1.7×10^{-1}	1.9×10^{-3}	1.8×10^{-3}	$<1 \times 10^{-4}$

electrode, with two austenitic stainless steel pieces (JIS-SUS316) 25 cm^2 in surface area as counter electrodes. The ACM522 working electrode was centered between the two parallel stainless steel counter electrodes; the distance between the parallel counter electrodes was 6 cm. Before PEO, the ACM522 substrates were polished through successive grades of silicon carbide abrasive papers from 180 to 2000, followed by buffing with 3 μm and 1 μm diamond pastes. PEO was carried out with a direct-current power supply (Takasago Ltd., ZX-400H) at 30 mA cm^{-2} in an aqueous solution containing 0.50 mol dm^{-3} (M) trisodium phosphate dodecahydrate ($Na_3PO_4 \cdot 12H_2O$), the pH of which was about 13. The temperature of the electrolyte was kept at 20 °C using a water bath.

The morphology of PEO films was observed using a field emission scanning electron microscope (JEOL Ltd., JSM-6500F). The structure of the PEO films was investigated using X-ray diffraction (XRD; Rigaku, RINT-2000) with a Cu X-ray tube. The composition of PEO films was analyzed with an X-ray photoelectron spectrometer (JEOL Ltd., JPS-9010TRX) with Ar$^+$ ion sputtering accelerated at 500 V. The polarization curves of PEO-treated ACM522 substrates were measured at 1.0 mV s^{-1} in a 3.5 wt.% sodium chloride (NaCl) aqueous solution at 25 °C with a potentiostat/galvanostat (Hokuto Denko Co., Ltd., HA-151) using a Ag/AgCl electrode in 3.33 M potassium chloride solution (Horiba 2565A-10T: 0.206 V vs. SHE at 25 °C) and a platinum plate (20 × 20 mm) as the reference and counter electrodes, respectively. The cathodic and anodic curves were measured separately from the immersion potential to the cathodic direction first, and then from the immersion potential to the anodic direction. The time dependence of the impedance of PEO films was investigated by electrochemical impedance spectroscopy using a potentiostat/galvanostat with frequency response analyzer (Princeton Applied Research, AMETEK, Inc., VersaSTAT 3) at an amplitude of 10 mV and frequency range of 0.1 MHz to 0.1 Hz using a platinum plate counter electrode (20 × 20 mm). Salt spray tests were conducted using a salt spray test instrument (Suga Test Instruments Co., Ltd., STP-90V-2); 50 g dm^{-3} NaCl aqueous solution was sprayed onto samples at 35 °C. The spray amount was 0.125–0.25 mm h^{-1}.

3. Results

Fig. 1 shows the voltage variation during PEO; treatment times that characterize different voltage behavior are marked on the curve. The voltage behavior is reproducible; the only slight change is in the gradient after 300 s. The voltage increases throughout the reaction, but the increase changes with treatment time; the voltage behavior can be classified into four stages. In the first stage, the applied voltage steeply increases up to about 140 V. In stage II, the voltage only increases slightly, remaining almost constant around 150 V. In stage III, the voltage starts to gradually increase again to about 200 V, and finally, the voltage randomly oscillates between 100 V and 250 V in stage IV. The changes in voltage correspond to changes in electrical resistance of the PEO-treated ACM522 substrates. Different discharge sparking was observed during different stages of PEO. Many minute discharge sparks flickered on the whole surface in stage I, and a small discharge spark emerged and moved around the surface in stage II. In stage III, many small discharge sparks flickered again on the whole surface, while in stage IV, a relatively large long discharge spark was locally observed along with many associated small sparks on the whole surface.

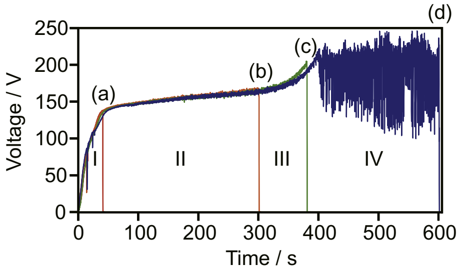

Fig. 1. Voltage variation during PEO in 0.50 M sodium phosphate aqueous solution at 30 mA cm^{-2}. Times marked are: (a) 45 s, (b) 300 s, (c) 375 s, and (d) 600 s.

The cross-sectional scanning electron microscope (SEM) images of the PEO-treated ACM522 substrates at the end of each stage are displayed in Fig. 2. It turns out from Fig. 2 that two kinds of film were formed by the PEO process, as discussed below. A thin film (1 μm thickness) forms first, during stage I. In stage II, the second film (external PEO film) is formed on the thin first film (internal PEO film). The thickness of the external PEO film is not uniform, and there are some areas where the external PEO film does not completely cover the internal PEO film (Fig. 2b)). Therefore, the electrical resistance of the substrate does not increase very much in stage II, and hence the applied voltage is almost constant. In stage III, the external PEO film continues to develop, and the covering is gradually completed, resulting in the increase in applied voltage. The external PEO film increases in thickness to larger than 40 μm in stage IV, although the applied voltage randomly oscillates because of local breakdown of the PEO film as shown in Fig. 1. Fig. 3 shows SEM images of the surface of the PEO-treated ACM522 substrates. The internal PEO film has a porous morphology (Fig. 3a) the external PEO film, which has a melted-like appearance with fewer cracks, gradually covers the whole surface of the internal PEO film as treatment continues. Generally, normal electrolytic oxidation of ACM522 results in an oxide film with many cracks, and the external PEO film with its melted-like appearance and fewer cracks is preferable for corrosion-proofing.

Fig. 4 shows XRD profiles of the PEO-treated ACM522 substrates. Only peaks from metallic magnesium are seen in the profile of the substrate treated for 45 s, where only the porous and thin internal PEO film has formed. In contrast, peaks from monoclinic $Mg_3(PO_4)_2$ are observed in profiles of the substrates treated for 300 s, 375 s and 600 s, indicating that the external PEO film is mainly composed of monoclinic crystalline $Mg_3(PO_4)_2$. The compositions of the PEO films obtained at 45 s and 375 s were analyzed by XPS, and the results are listed in Table 2. As described above, the PEO film obtained at 45 s corresponds to the internal PEO film, while the PEO film obtained at 375 s contains both the internal and external PEO films. According to Table 2, the concentrations of Mg, O, P, Ca, Ce, and La do not change with etching time in both cases. On the other hand, the concentration of Na decreases with etching time and that of Al increases. Comparing the compositions of the internal and external PEO films shows that the concentrations of Ca, Ce and La are lower and that of Al is higher in the external PEO film than in the internal PEO film, indicating that alloy constituents other than Al tend to dissolve in the electrolyte during PEO. The external PEO film is also rich in electrolyte constituents P and