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Effect of phytic acid on the corrosion inhibition of composite film coated on Mg–Gd–Y alloy

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ABSTRACT

A new composite film (named as PSPF) was prepared by depositing layers of plasma electrolysis oxidation (PEO) film, self-assembled nanoparticle containing phytic acid film and fluorocarbon paint on a Mg–Gd–Y alloy. The effect of phytic acid on the corrosion inhibition property of the PSPF film was investigated by various analytical instruments and methods. Based on the results, the PSPF film showed enhanced barrier properties and that could be used to provide good protection against corrosion. In addition, the strong adhesion properties of the PSPF film was another important attribute for promising long-term service performance in a corrosive neutral salt environment.

1. Introduction

Plasma electrolytic oxidation (PEO) has been widely used to apply a bilayer (an outer porous layer and an inner barrier layer) of ceramic films on Mg and its alloys. Following the application of PEO process on Mg and its alloys, a great enhancement is seen in its properties including wear resistance, corrosion resistance, mechanical strength and electrical insulation [1–3]. However, when compared to the compact barrier layer of PEO film, the outer porous layer is very weak, and so it acts as a transportation route for the corrosive ions to enter the barrier layer of the PEO film. This inherent problem in PEO film could be solved by forming a composite film by cataphoresis and painting, although effective long-term corrosion protection of the Mg substrate in a practical service environment cannot be guaranteed. The main reasons for not being able to achieve a long-term corrosion protection are as follows: (1) the poor compatibility between the top paint and the PEO film which contributes to a large difference in the elastic ratio and linear expansion factor, and (2) the poor adhesion between the conventional paint and PEO film. Under these unfavorable conditions, the composite film's properties are greatly affected by bubbling, flaking, cracking, and peeling caused by the service environment.

In recent years, an environmentally friendly organic–inorganic hybrid system of self-assembled nanoparticles (SANP) was invented [4–12]. Based on the previous work [13], we prepared a composite film for protecting films comprising of the SANP and the PEO films on the surface of a Mg alloy substrate through the following processes as described below. First, the aqueous sol–gel process was used to produce the silica nanoparticles by hydrolysis of epoxy silanes. Next, the silica nanoparticles containing silanol (SiOH) and epoxy functional groups penetrated into the pores of the PEO film. Finally, a crosslinking agent for amines was added into the SANP solution to produce a large-scale and strong Si–O–Si network by the crosslinking reaction between the amine and the epoxy functional groups of hydrolytic nanoparticles. Moreover, the silanol (SiOH) functional groups formed an interface with a higher density of Mg–O–Si bonds by reacting with the PEO film. Thus, the formation of composite film with good corrosion protection and adhesion properties were possible to the synergistic action of Si–O–Si and Mg–O–Si bonds. However, earlier we used a relatively strong organic acid–acetic acid in our SANP solution, which remained as a residue in the SANP films, and that eroded the Mg substrate by passing through the porous PEO film during a long-term practical service. To overcome the above disadvantage, we have replaced acetic acid with phytic acid in the recent work [14], and the results show promising corrosion protection due to the powerful chelating capability and good corrosion inhibitor properties of phytic acid [15–18].

The Mg–Gd–Y alloys have received much attention due to their high specific strength at elevated temperatures and their good

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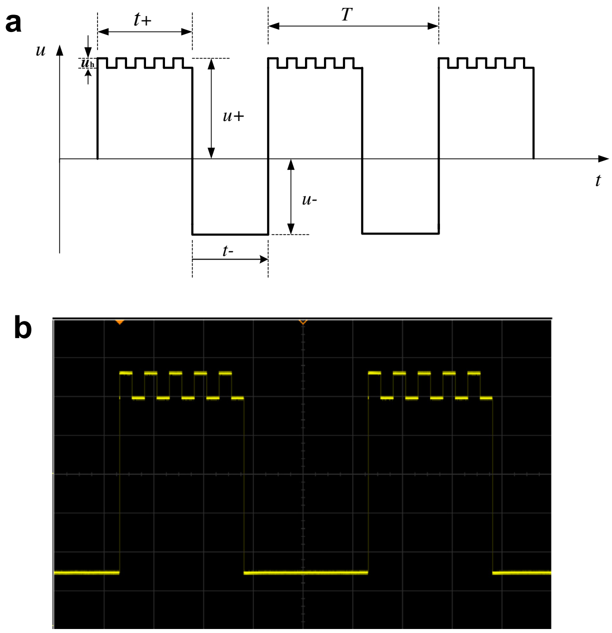

Fig. 1. (a and b)Oscillograms of the monopolar polar pulse carrier wave mode.

Table 1
Control parameters of MSV waveform and HFSV waveform.

MSV waveform			
$u-$ (V)	$t-$ (ms)	$u+$ (V)	$t+$ (ms)
−70	0.2	450	0.3
HFSV waveform			
u_{h-} (V)	u_{h+} (V)	f (Hz)	
40	40	1500–2000	

Table 2
Composition and operating conditions of SANP solutions.

Technique name		SANP solution with acetic acid	SANP solution with phytic acid
Technique abbreviation		SANP-A	SANP-P
Silane	Composition	GPTMS and TEOS	GPTMS and TEOS
	Mole ratio n(GPTMS):n(TEOS)	3:1	3:1
	Mixture time	15 min	1 h
Acid	Composition	Acetic acid	Phytic acid
	Mole concentration	0.05 mol/L, 5 ml	0.02 mol/L, 5 ml
	Dropwise duration	3 h	30 min
Solvent	Composition	H_2O and ethanol	H_2O and ethanol
	Mole ratio	10:1	30:1
	Hydrolytic time	72 h	150 h
Crosslink	Composition	TETA	TETA
	pH of SANP solution	5.5–6.5	5.5–6.5
	Crosslink time	30 min	10 min

Table 3
Preparation of composite films coated on the Mg–Gd–Y alloy substrates.

	Step	Thickness
PSAF	(1).PEO film	20 ± 1 μm
	(2) SANP-A film	400–600 nm
	(3) FC paint	10 ± 1 μm
PSPF	(1).PEO film	20 ± 1 μm
	(2) SANP-P film	400–600 nm
	(3) FC paint	10 ± 1 μm

Table 4
Composition and operating conditions of FC paint.

Step	Composition	Quantity (wt.%)
Paint mixing	Part A	70%
	Part B	15%
	Diluent	15%
Spray coating	Temperature	25 °C
	Spraying time	30 s
	Film thickness	10 ± 1 μm
	Drying time	24 h

creep resistance [19–21], however, they suffer from corrosion protection when exposed to air and moisture. In the present paper, a composite film comprising of PEO and SANP layers are employed to protect the Mg–Gd–Y alloy from corrosion. Further, the effect of phytic acid (also known as inositol hexakisphosphate) on the corrosion inhibition properties of the SANP and its corresponding composite films (PEO layer + SANP-P layer + fluorocarbon paint, PSPF) coated on the Mg–Gd–Y alloy substrates will be investigated.

2. Experimental

2.1. Preparation

Mg–Gd–Y alloy sheets (50 mm × 50 mm × 1 mm) were used as the substrate material for the surface treatments with the following composition (wt.%): Gd, 9.53%; Y, 1.45%; Zr, 0.7%; and Mg balance. The Mg sheets were degreased by ultrasonication in acetone, cleaned with distilled water, and then dried in air.

The PEO experiments were conducted by using a 100 kW power supply (Duercoat IV), which was able to deliver a monopolar polar pulse carrier wave mode. As shown in Fig. 1 and Table 1, this mode exported a complex square voltage waveform by loading a high-frequency square voltage (HFSV) waveform on a matrix square voltage (MSV) waveform. The PEO process was carried out in a two-electrode cell comprising of a Mg electrode and a graphite counter electrode. The electrolytes: KOH (180 g/L), Na_3PO_4 (40 g/L), and KF (35 g/L), were dissolved in de-ionized water at room temperature (25 °C). The PEO experiment time was completed in 20 min, and the temperature of the electrolyte was maintained below 35 °C during the entire process using a Durachill cooling system from Polyscience Co.

The SANP solution containing phytic acid (SANP-P) was formulated as shown in Table 2. Compared to the SANP solution containing acetic acid (SANP-A), the SANP-P solution was prepared by the hydrolysis reaction of 3-glycidoxypropyltrimethoxysilane (GPTMS) and tetraethoxysilane (TEOS) in de-ionized water for 1 h (mixing time). Subsequently, a solvent mixture of water (H_2O) and ethanol with a molar ratio of n(GPTMS):n(TEOS):n(H_2O):n(ethanol) = 3:1:30:1 was added to the above solution. Then phytic acid (0.02 M, 5 ml) was added dropwise to the stirred solution (30 min). After being hydrolyzed for 150 h at room temperature, the crosslinking agent triethylene tetramine (TETA) was added into the solution until a pH value between 5.5 and 6.5 was reached. After 10 min, the specimens were deposited in the SANP solution by controlling the withdrawal speed to 1 cm/min. Finally, the films were dried at room temperature for 30 min.

Table 3 shows the preparation of the two composite films composed of three layers: a primer layer of the PEO film, a middle layer