Corrosion Science 101 (2015) 201–207

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Short communication

Insights into plasma electrolytic oxidation treatment with particle addition

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ARTICLE INFO

Article history:
Received 13 April 2015
Received in revised form
18 September 2015
Accepted 19 September 2015
Available online 25 September 2015

Keywords:
A. Alloy
A. Magnesium
B. SEM
B. XRD
C. Oxide coatings

ABSTRACT

Plasma electrolytic oxidation (PEO) processing has received considerable attention for improving the corrosion or wear resistance of magnesium and its alloys. However, it cannot provide high-barrier long-term protection due to its high porosity. A novel approach is to introduce reactive particles to PEO coatings, aiming to seal the porosity and to provide wider range of coating compositions. Experiments with nano- and micro-sized SiO_2 particles and different concentrations of KOH in the electrolyte provide new insights into possible up-take and incorporation mechanisms of particles during PEO processing.

1. Introduction

Plasma electrolytic oxidation (PEO) is a promising surface treatment process to produce ceramic-like coatings on light metals (Mg, Al and Ti) and their alloys, with incorporation of species originating from the substrate and the electrolyte, for corrosion protection and wear resistance for biomedical applications [1–6]. The process accompanies a large number of short-lived microdischarges, caused by dielectric breakdown of oxide film at relatively high voltages, leading to coatings with high porosity. Some defects are generated by entrapped gas or rapid cooling after the sparks are extinguished. Thus, sealing or avoidance of the high porosity is essential to improve the coating properties. Particle addition into PEO coatings is a novel approach to obtain a type of in situ sealing. Arrabal et al. [7,8] fabricated coatings with ZrO_2 nanoparticle additions and assumed that the particles were transferred to the interface between the inner/outer layer through short-circuit paths in the outer layer. Lee et al. demonstrated that the electrophoretic mobility and mechanical mixing in molten magnesium oxide were main factors leading to particle incorporation [9]. Necula et al. [10] introduced Ag nanoparticles to PEO coating. They assumed that particles can be preserved in the coating after they are delivered and entrapped in the sites of coating growth. Up to now, the proposed particle incorporation theories are limited, as they only focus on nanoparticles and do not explain the principles for various incorporation regimes.

If particles are incorporated without a reaction or no new phase formation, it is considered to be an inert incorporation. The other possibility is reactive or partly reactive incorporation, when the particles melt through the high energy discharges and then react with other components from the electrolyte and the matrix. The melting point of the particles is one crucial factor to determine the incorporation mode. Generally, the plasma electron temperature during PEO process is above 3000 K [11,12], which is much higher than the melting point of the most frequently used particles [8,10,13–15]. Nevertheless, partly reactive or inert incorporation of the particles into the coating is normally observed. Thus, it may be deduced that the particle size is an important factor as the short-lived discharges may not be able to completely melt large particles. It is also generally known that nanoparticles have a lower melting temperature compared with the large particles of the same material [16,17]. However, various nanoparticles can still be incorporated inertly [13,18]. Hence, the nature of the particle itself, i.e., chemical stability and type of bonds, may determine the way particles participate in the PEO processing. For example, it is hard to achieve reactive incorporation for metallic particles (Ag), while it is more easily to realize for inorganic particles.

The present work investigates the influence of the amount and the size of SiO_2 particles, and MgO/SiO_2 ratio on the coating formation, aiming to understand the different mechanisms of particle

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http://dx.doi.org/10.1016/j.corsci.2015.09.016

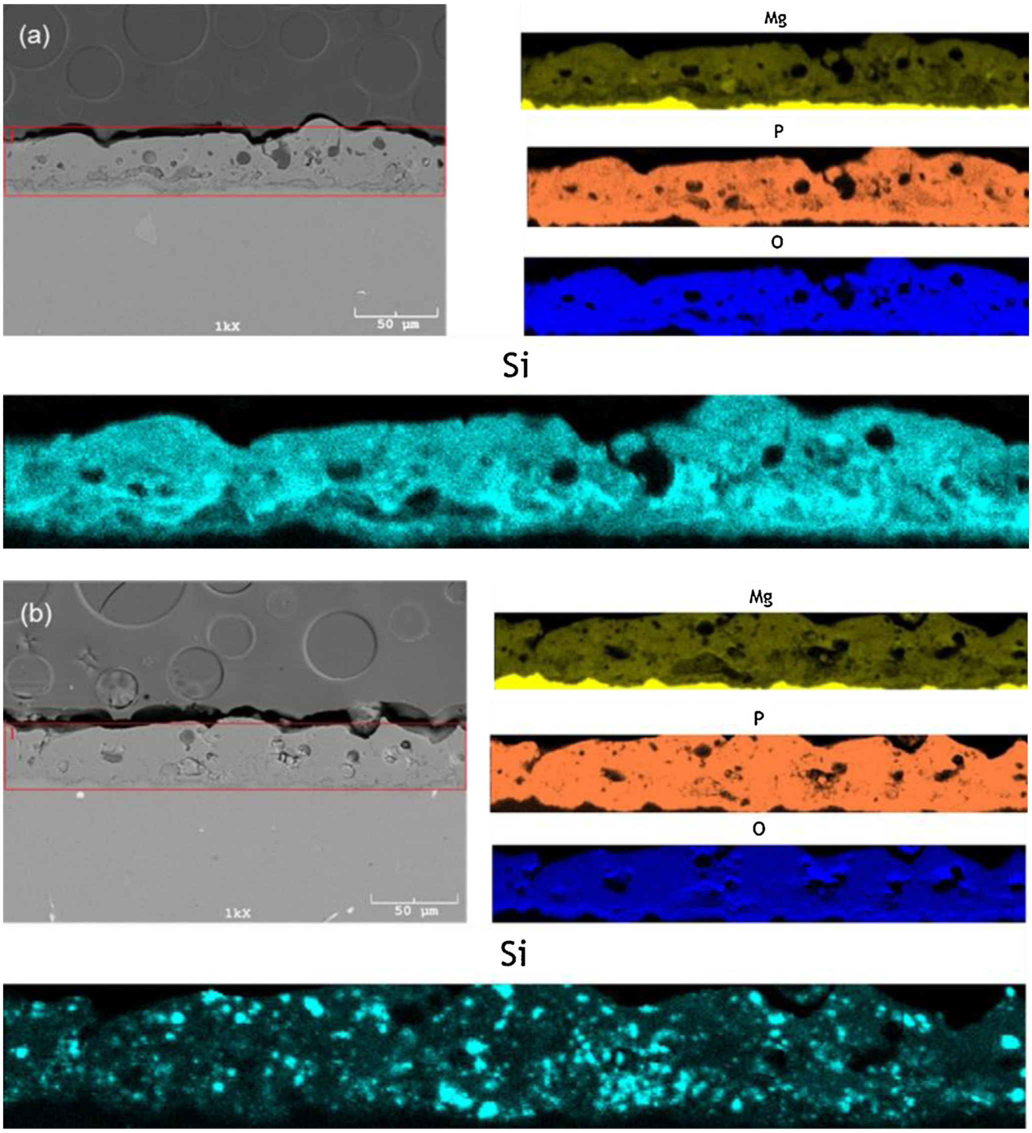

Fig. 1. SEM images of the cross section and Si mapping of the PEO coatings with particle addition (a) PEO (n), (b) PEO (μ).

up-take and incorporation based on analyses of the different coating microstructures and compositions.

2. Experimental

AM50 magnesium alloy samples with dimensions of 15 mm × 15 mm × 4 mm were treated by a pulsed DC power supply (t_{on}:t_{off} = 0.4 ms:3.6 ms) under constant voltage regime (450 V) for 10 min. The chemical composition of AM50 alloy, as measured with an Arc/Spark Optical Emission Spectroscopy system (Spark analyser M9, Spectro Ametek, Germany), is 4.74 wt.% Al, 0.383 wt.% Mn, 0.065 wt.% Zn, 0.063 wt.% Si, 0.002 wt.% Fe, 0.002 wt.% Cu and Mg balance. The electrolyte consisted of KOH (1 g/l), Na_3PO_4 (20 g/l) and 5 g/l SiO_2 particles with size of 12 nm avg. and 1–5 µm, respectively. Electrolytes with high concentration of KOH (8 g/l) were prepared to investigate the influence of the MgO/SiO_2 ratio on SiO_2 particles up-take (Table 1). PEO coatings without particle addition were produced for comparison. A stirrer and bubbling with compressed air were used to disperse particles uniformly. The temperature of the electrolytes was kept at 10 ± 2 °C using water cooling system. A scanning electron microscope (TESCAN Vega3 SB) equipped with EDS was used to examine the microstructure and composition of the PEO coatings. X-ray diffraction (XRD) investigations were conducted using a Siemens diffractometer operating at 40 kV and 40 mA with Cu Kα radiation.

Table 1
Electrolyte composition for PEO treatment.

Coating	KOH (g/l)	Na_3PO_4 (g/l)	SiO_2 (g/l, 12 nm)	SiO_2 (g/l, 1–5 µm)
PEO	1	20	–	–
PEO (n)	1	20	5	–
PEO (μ)	1	20	–	5
HPEO	8	20	–	–
HPEO ($n-2$)	8	20	2	–
HPEO ($n-5$)	8	20	5	–
HPEO ($\mu-2$)	8	20	–	2
HPEO ($\mu-5$)	8	20	–	5

3. Results and discussion

The cross-sections and EDS maps of the coatings with 5 g/l nano- and micro-sized SiO_2 particle addition are shown in Fig. 1. Mg, P, O and Si elements were detected as the main elements in both PEO