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Microstructural, protective, inhibitory and semiconducting properties of PEO coatings containing CeO₂ nanoparticles formed on AZ31 Mg alloy

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ABSTRACT

The aim of this study is to investigate the effects of presence of cerium oxide nanoparticles on the microstructure, protective properties and inhibitory properties, while also enquiring into plasma electrolytic oxidation (PEO) coatings semiconductors properties, which were formed in a phosphate electrolyte solution, applied on AZ31 Mg alloy. According to the SEM/elemental map, Ce has been deposited in the oxide coating structure, and results in the changing of the morphology and coating thickness. According to the results of potentiodynamic polarization (PDS) and electrochemical impedance spectroscopy (EIS), during the short and long immersion period of up to 16 days, the presence of optimum level of CeO₂ in the phosphate electrolyte solution (3 g/l) results in the highest protection properties for PEO coating. Furthermore, the EIS test following the PDS, indicated the inhibitory effects of the cerium products, while the results of Mott-Schottky (M-S) test indicated a decrease in the donor concentration with presence of optimum CeO₂ and thus, a drop in the tendency to undergo corrosion reactions. Thermodynamic investigations have shown that the formation of corrosion products which contain Ce is possible and stable, hence leading to the improvement of the protective properties of PEO coatings.

1. Introduction

Extraordinary mechanical and physical properties of magnesium (Mg) and its alloys have led to their widespread use in the automobile industry, aerospace, mobile phones, computer components, construction industry, and sporting goods [1–3]. However, high chemical activity or poor corrosion resistance, along with low wear resistance, limit its extensive use, especially in applications exposed to corrosive environments or to wear [4]. One of the best strategies to enhance the corrosion resistance of Mg alloys, is surface optimization using a variety of protective coatings such as anodizing, conversion coatings, electrochemical plating, PVD coatings and different types of organic coatings [5–9]. Many of the aforementioned methods, such as chromate conversion coatings, despite having great potential in providing adequate protection for Mg alloys, are highly toxic and carcinogenic, therefore their use is quite limited in industrial applications [10]. Some other methods, such as cerium conversion coating, due to its high porosity, are unable to provide sufficiently high corrosion resistance. Plasma electrolytic oxidation (PEO) is one of the protective coatings for Mg alloys. PEO process is an anodic plasma-chemical surface treatment. PEO coatings are formed by creating oxygen plasma in a slightly alkaline solution [11]. Localized melting and consequent solidification of the surface of the base metal lead to the formation of an oxide-ceramic

layer. Fabricated coatings usually have three parts, a thin barrier layer (~100 nm), oxide/ceramic layer with low porosity and a ceramic layer with high porosity. The final layer can act as a basis for improving the adhesion strength of paint or impregnation operations. Moreover, PEO process is able to create a uniform coating even on the edges and cavities [12].

Usually, the used electrolyte solutions for the application of coating on the Mg alloys with the PEO process are eco-friendly electrolyte solutions such as phosphate and silicate based electrolytes. By adjusting the parameters of process such as the type of the applied current and appropriate bipolar electric regime, the amount of pores in the external structure can be lowered and the thickness of the inner dense layer can be increased. However, the presence of pores in the PEO structure is inevitable, and it reduces the barrier properties of the formed coating, thus resulting in a drop in the corrosion protection properties of the coating. That is why various strategies are proposed in order to improve the protective properties of PEO coatings so as to prevent rapid degradation of the oxide coating [13,14]. Recent advances in improving the coating properties of PEO have been focusing on the use of various additives in their structure [15]. To further increase the corrosion resistance of the fabricated coatings, several studies in the field of PEO coatings containing compounds and stable oxides, such as TiO₂, SiO₂, ZrO₂ and Al₂O₃ by optimizing the composition of the electrolyte

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solution, have been carried out [16–18]. Adsorption process of the particles in the coating structure is complex, and depends on several factors such as particle concentration, size, mobility, sedimentation as well as parameters of process such as current density, processing time, the type of salt used in the electrolyte solution, anodic process steps and also the type of the base metal [19,20]. Nowadays, the majority of the researches are focused on the use of nano-sized particles. Various nanoparticles have been used for incorporation into the structure of PEO coatings. It has been reported that nanoparticles enter the structure through the short-circuit paths created throughout the process, and that the main volume of the nanoparticles is placed on the external porous layer [17,21]. Different results have been reported for the use of nanoparticles to improve the protective properties of PEO coatings. It could be due to the different characteristics of the PEO process for different researchers. For instance, it has been reported that incorporation of zirconia nanoparticles in the structure of oxide coating formed on the surface of AZ91 Mg improves corrosion resistance to a small extent [22]. The presence of ceria particles in the structure of PEO coatings on AZ31 Mg alloy slightly improves corrosion resistance of the coating [23]. It is even reported that the presence of some particles such as Si_3N_4 has no significant effect on improving the protective properties of the coating [24]. The reason for this phenomenon is the lack of sufficient attention to the self-healing properties of the coating and its role in improvement of the retention of protective properties. Various research results indicate that rare earth elements have corrosion inhibition effect [25,26]. They are used in anodizing or conversion coating, or improving the corrosion resistance of galvanized steel and nickel-base alloys [27,28]. Furthermore, some research have been carried out on the use of Ce containing compounds during the PEO process. For example, cerium nitrate is used as an additive in silicate based electrolytic for coating Mg, or cerium conversion coating is used as a pretreatment for PEO which causes the translocation of ceria in fabricated coatings [29]. Also, a number of research have been performed in the field of direct ceria particles incorporation during PEO process in a silicate based electrolyte solution, and the corrosion behavior of oxide coating containing ceria particles has been studied [30]. Mohedano et al. [15] examined the participation of ceria particles in chemical reactions during the formation of oxide coating in silicate based solutions.

Although various papers have been published on the usage of ceria particles to improve the corrosion resistance of the PEO coatings, no specific studies on the role of ceria nanoparticles as additive in the semiconductor properties of oxide coating have been carried out. Also, many aspects of the effects of ceria nanoparticles and their role in enhancing the protective properties of the coating have been largely neglected. For example, the inhibition role of ceria nanoparticles, corrosion resistance in long-time immersion as well as the stability of Ce ions reaction products with corrosive agents such as OH^- ions are not yet fully investigated.

The most important purpose of this paper is to systematically study the effects of varying amounts of ceria nanoparticles on the corrosion protection performance of PEO coatings applied on the surface of AZ31 Mg alloy in the phosphate based electrolyte solution using PDS and EIS tests, as well as the effect of ceria nanoparticles on the semiconductor properties of the coatings using Mott-Schottky analysis. The results obtained from electrochemical tests are qualitatively dependent on the semiconductor properties (flat band potential and donor concentration) of the coatings obtained from the Mott-Schottky analysis.

In this paper, inhibition mechanisms of ceria nanoparticles and their role in enhancing the corrosion resistance of PEO composite coatings were investigated using a set of microscopic and structural methods, complementary electrochemical techniques and thermodynamic calculations.

Table 1

Nominal chemical composition of AZ31 Mg alloy.

| Elements | Mg | Al | Zn | Mn | Si | Fe | Ni |
|----------|-------|------|------|------|------|-------|--------|
| wt% | 95.95 | 3.08 | 0.75 | 0.15 | 0.01 | 0.001 | 0.0003 |

2. Materials and methods

2.1. Samples and PEO process

Rectangular samples with the dimensions of $4 \times 2.5 \times 0.1 \text{ cm}^3$ were cut from AZ31 Mg sheets with nominal chemical composition presented in Table 1. The surface of the samples were polished by metallographic emery papers numbers 600, 800, 1200, and 1500 and then to ultrasonically degreased in acetone. Mg samples were washed with distilled water, and dried in air before performing PEO operations. PEO device was consisting of a DC power source (600 V, 2.5 A, 750 W), stainless steel chamber containing the electrolyte solution as cathode, water coolant flowing system to maintain the temperature of the process. Mg samples as the anode, were placed in the phosphate base electrolyte solution while being attached to a brass rod by a hole at the top. Based on trial tests, PEO process was performed at a constant current density of 100 mA/cm^2 for 10 min across all samples. 1, 3, 5, 7 g/l of ceria nanoparticles were used as an additive. TEM image of ceria nanoparticle is shown in Fig. 1. As can be observed, the size of nanoparticles is $< 25 \text{ nm}$. For homogeneous distribution of the ceria nanoparticles in the electrolyte solution, the nanoparticles were added to distilled water and stirred for 24 h. Afterwards, prior to the addition of Na_3PO_4 and KOH, the solution was subjected to ultrasonication treatment for 1 h. Moreover, the solution was stirred using a magnet during the PEO process. The chemical composition of the electrolyte solution used in this study, along with the abbreviated name of the samples, is shown in Table 2. The pH and conductivity values of the electrolyte solutions with various concentrations of the ceria nanoparticles were measured by a pH meter (SANA SL-901), and a conductivity instrument (SPIRAX SARCO). The results are presented in Table 2. It is observed that all solutions have almost the same level of alkalinity and conductivity.

2.2. Characterization

Top surface and cross section of oxide coating were studied by scanning electron microscopy (SEM, Philips XL30). To view cross-sectional images of the oxide coating, the coating must be embedded in epoxy resin. After complete crosslinking, coating samples were

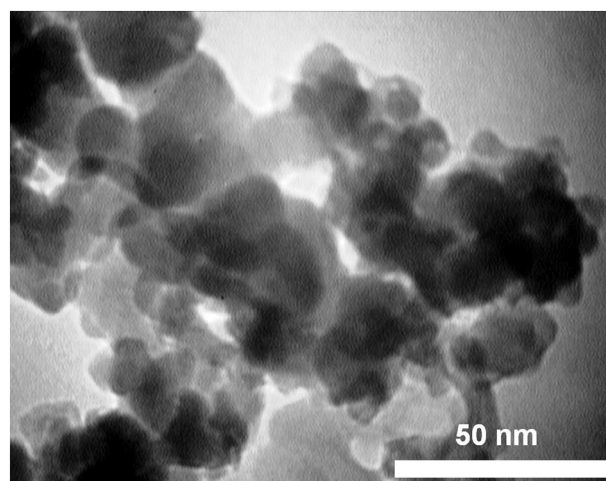


Fig. 1. TEM images of ceria nanoparticles used as additive in PEO electrolyte.

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