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Review

Plasma electrolytic oxidation of magnesium and its alloys: Mechanism, properties and applications

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Abstract

Plasma Electrolyte Oxidation (PEO) process has increasingly been employed to improve magnesium surface properties by fabrication of an MgO-based coating. Originating from conventional anodizing procedures, this high-voltage process produces an adhesive ceramic film on the surface. The present article provides a comprehensive review around mechanisms of PEO coatings fabrication and their different properties. Due to complexity of PEO coatings formation, a complete explanation regarding fabrication mechanisms of PEO coatings has not yet been proposed; however, the most important advancements in the field of fabrication mechanisms of PEO coatings were gathered in this work. Mechanisms of PEO coatings fabrication on magnesium were reviewed considering voltage–time plots, optical spectrometry, acoustic emission spectrometry and electronic properties of the ceramic film. Afterwards, the coatings properties, affecting parameters and improvement strategies were discussed. In addition, corrosion resistance of coatings, important factors in corrosion resistance and methods for corrosion resistance improvement were considered. Tribological properties (important factors and improvement methods) of coatings were also studied. Since magnesium and its alloys are broadly used in biological applications, the biological properties of PEO coatings, important factors in their biological performance and existing methods for improvement of coatings were explained. Addition of ceramic based nanoparticles and formation of nanocomposite coatings may considerably influence properties of plasma electrolyte oxidation coatings. Nanocomposite coatings properties and nanoparticles adsorption mechanisms were included in a separate sector. Another method to improve coatings properties is formation of hybrid coatings on PEO coatings which was discussed in the end.

Keywords: Plasma electrolytic oxidation; Magnesium; Tribological properties; Biomedical properties; Nanocomposite coatings

1. Introduction

Magnesium and its alloys are among the lightest group of engineering metals. Magnesium also has very good properties such as low density, high strength to weight ratio, tremendous dimensional durability [1–5], good electromagnetic shielding, higher damping capacity and high machinability. Hence, magnesium and its alloys have found many applications in various industries including automobile, aerospace and communications [6]. However, high activity of magnesium weakens corrosion and wear resistance of this metal and its alloys especially in corrosive media [7–14]. A proper surface treatment may improve wear and corrosion resistance of the substrate. There are some surface treatment techniques established for protection of magnesium and its alloys. These techniques include chemical conversion plating, electrodeposition, anodizing, gas-phase deposition, organic coatings and sol-gel technique [15,16]. A popular technique for surface treatment of magnesium and its alloys is plasma electrolyte oxidation which is likewise recognized as micro-arc oxidation [17,18], micro-plasma oxidation [19] and anodic spark deposition [20]. Originating from traditional anodizing process, PEO is a rather inexpensive and environmentally friendly technique [21,22]. It is a high-voltage process that is broadly used for surface treatment of magnesium and its alloys [23–30]. In this process, plasma discharge occurs which leads to partial fusion of an oxide film and consequently formation of an extremely adhesive oxide coating on the substrate [31]. The produced coatings

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possess very good wear and corrosion resistance as well as proper electrical properties and high thermal stability [32–34]. There have been many studies on PEO coatings on magnesium. Considering the fact that a comprehensive review article around PEO coatings on magnesium has not been published in recent years, the aim of the present text is to provide a full understanding on all aspects of this process. First, morphologies of all phases formed during the process were discussed. Afterwards, coating formation mechanisms were comprehensively studied and then different properties of coatings including corrosion resistance, tribological properties, biomedical properties and effects of various parameters were considered. Finally, nanocomposite and hybrid coatings produced by PEO process were investigated.

2. Surface morphology and different phases formed on magnesium substrate in PEO process

Microstructural characteristics of PEO coatings depend on operational conditions, and coatings thickness may vary between 5 and 200 µm. Generally, the coating interface is in a zigzag form which makes the coating seem integrated into the substrate. PEO process consists of a plasma discharge procedure around an immersed metal in an environmentally friendly electrolyte. Discharge procedures significantly affect coatings structure and consequently their physical and mechanical properties [35]. Three processes occur simultaneously in the PEO treatment. These include electrochemical and plasma chemical reactions as well as oxygen thermal diffusion. It is believed that PEO coatings on magnesium substrates possess three-layer structures [36]. Fig. 1(a) and b show SEM micrographs of a coating surface and cross section, respectively. A schematic design of the outer porous layer, the fairly compact layer in the middle and the thin and compact layer (barrier layer) that sticks well to surfaces is presented in Fig. 1(c). Although the compact middle layer is responsible for good mechanical properties (wear resistance) and corrosion resistance, the compact middle layer provides excellent corrosion resistance in coatings [37]. Surface of PEO coatings generally include pancake-form structures with a discharge channel in the center of each pancake. Molten substances effuse through the discharge channels and quench while being exposed to the cold electrolyte. In results, distinct boundaries would develop which separate the pancake [38]. Rather large voids at the center of each pancake indicate extreme discharge which may also penetrate deep into the coatings. Pore size is a function of discharge density as well as process time. It is reported that the pore diameter in magnesium alloys is usually between 0.5 are 50 µm. Discharge channels are surrounded by molten substances and local micro cracks. Formation of micro cracks may be due to quenching of molten substances while being exposed to the cold electrolyte. Extreme discharges possess high input energies which causes fusion of considerable parts of the oxide film and substrate. Finally, molten substances flow out toward the surface and form large ceramic particles while they reach the cold electrolyte. Molten oxides around the pores show the fact that momentary temperature inside the micro-voids may reach several thousand degrees [39]. Yerokhin et al. [40] stated that this temperature may be around 2300 to 3000 K.

The nature of each phase that is formed in PEO process depends on the substrate and electrolyte type and species in the electrolyte. In PEO processes, the magnesium substrate is placed as anode in silicate based electrolytes; thus, magnesium dissolution reaction occurs under a strong electric field producing magnesium ions.

$$Mg \rightarrow Mg^{2+} + 2e^{-} \quad (1)$$

Formation of oxide films on magnesium is due to outward diffusion of magnesium ions and inward diffusion of SiO_3^{2-},

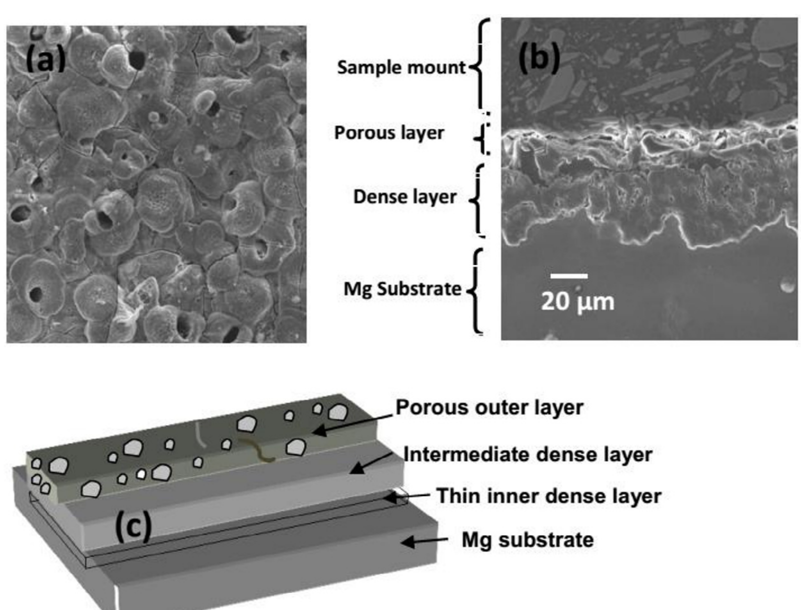

Fig. 1. Schematic of a) PEO coating surface b) cross section and c) different layer of PEO coating [36].

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