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The influence of current density on the morphology and corrosion properties of MAO coatings on AZ31B magnesium alloy

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ABSTRACT

Micro-arc oxidation (MAO) coatings were prepared on AZ31B magnesium alloy using alkaline silicate electrolyte at different current densities (0.026, 0.046 and 0.067 A/cm^2). Field Emission Scanning Electron Microscopy (FESEM) analysis of the coating revealed an irregular porous structure with cracked morphology. Compositional analysis carried out for MAO coating showed the presence of almost an equal amount of Mg and O (34 wt.%) apart from other elements such as F, Si and Al. The cross-sectional FESEM images clearly portrayed that the MAO coating was dense along with the presence of very few fine pores. The surface roughness (R_a) of the coatings increased with an increase in the current density. Potentiodynamic polarization and electrochemical impedance spectroscopic (EIS) studies were carried out for both the bare and MAO coated AZ31B Mg alloy in 3.5% NaCl solution. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) values obtained for the bare substrate were −1.49 V and 46 μA/cm^2, respectively. The coating prepared at 0.046 A/cm^2 exhibited the lowest i_{corr} value of 7.79×10^{-10} A/cm^2 and highest polarization resistance (41.6 MΩ cm^2) attesting to the better corrosion resistance of the coating compared to other samples. EIS results also indicated almost similar corrosion behavior for the MAO coatings. Mott–Schottky analysis showed n-type and p-type semiconductor behavior for the oxide layer present on the bare magnesium alloy and MAO coatings respectively.

1. Introduction

Magnesium and its alloys are widely used in automotive, aerospace and communication industries due to their outstanding properties such as light-weight, good heat emitting property, high specific mechanical strength and good resistance against electromagnetic waves [1,2]. However, their poor corrosion and wear resistance restricts the usage specifically in harsh environments [3–5]. Therefore, surface modification of these alloys is mandatory to improve their corrosion and mechanical properties. There are many surface treatments such as conversion treatment, organic coating and anodic treatment that are used in practice to enhance the properties [6]. Among these methods, micro-arc oxidation is an environment friendly surface treatment technique which provides high hardness, better corrosion and wear resistance properties for the Mg alloys [7,8].

Several parameters such as electrolyte composition, applied current density and process duration, play an important role in the development of oxide coating with excellent mechanical properties and improved corrosion resistance [9,10]. Studies have been reported on the effect of electrolyte and its concentration on the structure and properties of the MAO coating [11,12]. Smooth and compact MAO coating on AZ 31B Mg alloy has been obtained by the addition of benzotriazole (BTA) in silicate based electrolyte which exhibited improved corrosion resistance [13]. Incorporation of cerium oxide particles in MAO coated AZ 31B Mg alloy also exhibited a significant improvement in the corrosion resistance [14]. However, very few reports are available on the effect of current density on the properties of MAO coatings [15,16]. Srinivasan et al. [15] have reported that the coating prepared on AM50 Mg alloy at lower current density exhibited better corrosion resistance as compared to that at higher current density. They have demonstrated that the thickness, porosity, roughness of the MAO coating increased with increase in current density, and thereby influenced the corrosion resistance in chloride environment. Yue et al. [16] investigated the corrosion behavior of MAO coating prepared on AZ91D Mg alloy at three different current densities and observed that the coating prepared at higher current density exhibited good corrosion resistance due to the lower surface roughness and compactness as compared with the other coatings. Differing results have been reported on the effect of current density on MAO coating formation which affects the corrosion resistance. Therefore, there is a need to understand the influence of current density on the corrosion behavior of the MAO coatings.

In the present study, MAO coatings have been prepared on AZ31B Mg alloy by varying the current density using silicate based alkaline electrolyte. The developed coatings have been characterized for their structure, morphology and roughness. The electrochemical corrosion

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behavior of the coatings has been studied by potentiodynamic polarization and EIS techniques. An attempt has been made to understand the capacitance behavior of the oxide film by Mott–Schottky analysis.

2. Experimental

Commercially available AZ31B Mg alloy of dimensions 20 mm × 50 mm × 2 mm, was used as a substrate for the micro-arc oxidation process. Its composition is Al − 2.5%, Zn − 1.4%, Ca − 0.04%, Cu − 0.05%, Fe − 0.005%, Mn − 0.2%, Ni − 0.005%, Si − 0.1% and the rest being magnesium. Prior to coating, the samples were ground using emery abrasive papers, ultrasonically cleaned in trichloroethylene, rinsed with distilled water and dried. The pre-treated specimens were then subjected to micro-arc oxidation and the details are given in the Table 1. The variation of voltage with respect to treatment time was recorded. After the MAO treatment, the specimens were cleaned ultrasonically in trichloroethylene, rinsed with distilled water, dried and used for further studies.

The surface and cross-section morphologies and compositional analysis were examined using Field Emission Scanning Electron Microscopy equipped with Energy Dispersive X-ray Analysis (FESEM/EDAX model-Carl Zeiss Supra 40 VP) and also using a Nikon SLR camera. A 3-D profilometer, model Nanomap 500LS, was employed for the surface roughness analysis of as-prepared specimens. Metallographic cross-sectional MAO samples were prepared by depositing electroless nickel coating as a back-up layer. X-Ray diffraction (XRD) measurements of the substrate and coatings were made in as prepared condition with a Rigaku D/max 2200 powder diffractometer using Cu K_α radiation.

Electrochemical methods such as polarization and EIS measurements were carried out to evaluate the corrosion resistance of the MAO coating. These measurements were performed using AUTOLAB PGSTAT 302N potentiostat/galvanostat electrochemical system. The conventional three electrode cell was used. The sample to be investigated was used as a working electrode and Pt foil of about 1 cm^2 was used as a counter electrode. A saturated calomel electrode (SCE) was used as a reference electrode. All the measurements were carried out in 3.5% NaCl solution under open air condition. The samp
le was immersed in the corrosive medium (3.5% NaCl, pH 6.7) for about 30 min to attain the open circuit potential (E_{OCP}) or the equilibrium potential or steady state potential after which the impedance measurements were conducted using a frequency response analyzer (FRA). The spectrum was recorded in the frequency range of 10 mHz–100 kHz and the amplitude voltage of 10 mV on the E_{corr}. The impedance data was displayed as Nyquist and Bode plots. After EIS measurements, the system was allowed to attain its stable open circuit potential. After reaching the stable open-circuit potential, the upper and the lower potential limits of linear sweep voltammetry were set at −200 mV cathodic and +500 mV anodic with respect to the E_{OCP}. The sweep rate was 1 mV/s and the Tafel plot was obtained after the electrochemical measurements. The corrosion potential (E_{corr}), corrosion current density (i_{corr}) and polarization resistance (R_p) were deduced from the Tafel plot (i.e., log i versus E plot). The corrosion current was obtained using the Stern–Geary equation [17] and the corrosion rate (CR) was determined using the Faraday's law [18], namely, $CR = K(i_{corr}/\rho)EW$ where CR is given in mm/year, $K = 3.27 \times 10^{-3}$ mm g/μA cm year, ρ the density of the substrate (g/cm^3) and EW is the equivalent weight of the substrate. Mott–Schottky experiments were done by measuring the frequency response at 1 kHz during a 25 mV/s potential scan from −1.8 to 0.2 V. Mott–Schottky plot is a plot of (C_{sc}^{-2}) versus E, where C_{sc}^{-2} is the Capacitance in the space charge region and E is the potential.

Table 1
Composition and operating conditions of MAO coating on AZ31B Mg alloy.

Bath composition	Concentration
Na_2SiO_3	10 g/L
NaOH	1 g/L
NaF	6 g/L
Operating conditions	
pH	11
Temp.	25 °C
Coating duration	15 min
CD (A/cm^2)	0.026, 0.046, 0.067

3. Results and discussion

3.1. Surface morphology

Fig. 1(a–c) shows the surface morphologies of MAO coatings formed at different current densities (at 1000×) along with the back scattered images (at 5000×) as an inset. In the following text the MAO coatings prepared at different current densities such as 0.026, 0.046 and 0.067 A/cm^2 will be referred to as P1, P2 and P3 respectively. From the figures it is evident that the variation in the current density affects the morphology of MAO coating. The coating prepared at lower current density (P1) exhibits a relatively uniform surface appearance with a high degree of porosity. As the current density is increased, the porosity of the coating is decreased, though the diameter of the pores is increased which is evident from the back scattered image (inset of Fig. 1c). It has been reported that as the current density increases, the surface of the coating becomes coarser, rougher and in addition the thickness also increases. If the formed oxide layer is thicker, higher energy is required for the current to pass through the coating. Under these circumstances, the current is localized at weak points of the oxide layer to find its way through the coating. In addition, the surface structure of the coating develops cracks owing to the thermal stresses that are generated by rapid solidification during the process and the cracks on the surface generally grow with an increase in current density [19]. A similar observation has been reported by Srinivasan et al. that the size of the pore increases with an increase in current density with reduced pore density [15]. On the other hand, Yue et al. have reported that the roughness and porosity of the coating decrease with an increase in the current density, which is in contrast to the present study. According to the authors, at higher current density a large number of micro-pores sinter together and result in smaller dimension discharge channels, which in turn lower the surface roughness [16].

The cross-sectional images of P1, P2 and P3 coatings are shown in the Fig. 2. The MAO coating shows two distinct layers namely the dense inner layer and porous thick outer layer as shown in the figure. It has been mentioned in the literature indicating the presence of two distinct inner and outer layers in the cross-section of the coating [20,21]. The average thickness of the P1 coating is about 6 μm, whereas the P2 and P3 coatings have the thicknesses of about 12 and 10 μm respectively. Protrusions are not seen near the surface of P1 coating which clearly indicates the presence of shallow pores with smaller diameter and high pore density. As the current density is increased, the thickness of the coating is increased (P2) and a further increase in the current density shows a decrease in the thickness (P3). In general, increase in current density increases the thickness of the MAO coating due to the linear relationship between the current density and the thickness of the coating [3,15]. However, the thickness is also depends on the rate of dissolution of Mg and rate of formation of Mg oxide coating. If the dissolution rate is higher than the formation rate (above the optimum condition), thickness of the coating may decrease with increasing in the current density. The decrease in thickness of P3 coating may be due to the more dissolution of the Mg/formed coating rather deposition. The cross-sectional image of P3 coating also shows the presence of deep pores with cracks. From the above observations it can be seen that the P2 coating exhibits an optimum thickness along with roughness. Apart from that the pores seen in the P2 coating are not continuous.