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Chromate and HF free pretreatment for MAO/electroless nickel coating on AZ31B magnesium alloy

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ABSTRACT

Micro arc oxidation (MAO) coating was developed as an interlayer for the electroless nickel (EN) top coat to improve the corrosion resistance of Mg alloy. Prior to the electroless nickel deposition, oxide layer was activated by using $NaBH_4$ solution as a replacement for conventional chromate and HF activation processes. EN coatings were prepared using the alkaline carbonate bath. As-prepared coatings were characterized for the surface morphology and composition using Field Emission Scanning Electron Microscopy (FESEM) attached with energy dispersive analysis of X-ray (EDX). Potentiodynamic polarization studies were carried out in non-deaerated 3.5% NaCl solution to find out the corrosion resistance of the coatings. The MAO coating showed porous morphology with micro cracks whereas, MAO/Ni-P coating exhibited dense nodular structure. The cross-Ni-P and MAO/Ni-P/Ni-W-P duplex al images showed good adhesion between MAO and Ni-P layers. This clearly indicates that the present activation process results in dense with uniform pores of MAO coating along with excellent bonding at the interface for Ni-P coat. The MAO/EN coating combination showed two orders improvements in corrosion resistance as compared with the substrate.

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1. Introduction

In recent years, to take advantage of light weight and strength properties of Mg alloys, various surface treatments and coating systems have been developed primarily to improve the corrosion resistance [1]. Among the coating systems, electroless nickel (EN) plating is widely used for Mg alloys to improve the corrosion and wear resistance properties [2–5]. To obtain an adherent and uniform coating on difficult to plate Mg alloys, the use of chromate and HF pretreatments are mandatory [6–9]. However, strict environmental regulations restrict their usage because of hazardous nature. The expensive palladous activation treatment is a well-known process as a replacement for chromate-HF pretreatments for Mg alloys [10–12]. It has been reported that EN plating has been carried out over Mg alloys using tannic acid based conversion coating followed by HF treatment [13]. The formation of an intermediate oxide layer by electrolytic methods is also one of the ways these toxic pretreatments can be avoided [14–16]. Micro-arc oxidation (MAO)/EN coating, prepared using chromic acid and HF pretreatment has also been reported [17]. Junming Li et al. have developed EN coating with various morphologies using a pyrophosphate based bath over MAO pretreatment layer in different solutions over AZ31B Mg alloy. They adopted $SnCl_2$ and $PdCl_2$ sensitization and activation

procedures respectively over MAO layer for the deposition of Ni-P coating [15]. From the above reported literature, it can be clearly seen that for the activation of inert MAO layer to deposit electroless nickel coating, the hazardous chromate/HF and highly expensive $PdCl_2$ activation processes were followed.

It is well known that borohydride is a strong reducing agent and used for the deposition of NiB coatings. In the present investigation, an attempt has been made to utilise the borohydride in the pretreatment process for the reduction of Ni^{2+} over MAO interlayer which provides nucleation sites for the deposition of Ni-P coating. The systematic studies have been carried out to develop Ni-P coating on AZ31B Mg alloy with an MAO inter layer. The developed MAO/Ni-P coating system has been characterized for its composition, surface morphology and corrosion behavior.

2. Experimental

Commercially available AZ31B Mg alloy of dimensions 20 mm × 50 mm × 2 mm, were used as a substrate for micro-arc oxidation process. Prior 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 in the electrolyte containing 10 g/L Na_2SiO_3, 6 g/L KF and 1 g/L KOH. With the stirring and cooling process in action, the MAO process was carried out for 10 min under a constant current

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Table 1
Composition and operating conditions of the electroless nickel coating on AZ31B Mg alloy.

Bath constituents	Compositions
NiCO$_3$	10 g/L
HF(48%)	9 ml/L
Citric acid	5 ml/L
NH$_4$HF$_2$	10 ml/L
Na$_2$H$_2$PO$_2$·H$_2$O	20 g/L
NH$_3$·H$_2$O	30 ml/L
Operating conditions	
pH	7.1
Temp	82 ± 2 °C
Time	45 mins

density of 0.04 A/cm^2. Electrolyte temperature was maintained below 40 °C. The further details of MAO coating is discussed elsewhere [18]. After the MAO treatment, the specimens were rinsed with distilled water, dried and weighed using analytical balance. The oxide specimens were immersed in a mild alkaline bath for about 15 min, at 70 ± 2 °C to remove the soil contaminants. The bath composition of mild alkaline solution is a mixture of 45 g/L NaOH and 10 g/L Na$_3$PO$_4$. The pH of the solution is about 12.5 ± 0.2. The sample was washed thoroughly with distilled water. The surface activation was conducted by immersion of the pretreated oxide coating in the 100 mL electroless nickel solution for 2–5 min at room temperature followed by immersion in the NaBH$_4$ solution for forming the active sites (Ni^0 clusters). After the activation process, the sample was rinsed with the distilled water. The electroless nickel plating was achieved by dipping into the plating solution at 80 °C for 1 h. Then, the coated samples were cleaned with distilled water and dried and weighed. The composition of the electroless nickel plating solution can be found in Table 1. The duplex Ni-P/Ni-W-P coatings were prepared from the electroless nickel bath with addition of sodium tungstate (12 g/l). The pH values were adjusted using ammonia solution. The whole activation process including pretreatment, activation and plating are illustrated in Fig. 1.

The Surface morphology was examined using Field Emission Scanning Electron Microscopy (FESEM model-Carl Zeiss Supra 40 VP) and also Nikon SLR camera. A 3-D profilometer, model Nanomap 500LS was also 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.

The X-ray photoelectron spectra were recorded with a SPECS spectrometer equipped with a non-monochromatic AlKα X-ray excitation source (1486.6 eV) operated at 150 W (12 kV and 12.5 mA). The binding energies (EB) reported here were calculated with reference to C 1 s peak at 284.5 eV with a precision of ±0.1 eV. All the spectra were obtained with pass energy of 25 eV and step increment of 0.05 eV. Sputtering was carried out by defocused Ar$^+$ ion beam using QE11/35 ion gun by applying energy of 1 keV with Ar gas pressure of 1×10^{-5} Torr for 5

and 20 min. The experimental data were curve-fitted into several components with Gaussian–Lorentzian peaks after subtracting Shirley background employing CasaXPS program. For component peaks, slightly different full width at half maxima (FWHM) were used for metal and oxides. Asymmetry lineshapes were considered for metal components during curve fitting.

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 302 N 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 sample was immersed in the corrosive medium 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 plot. 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).

3. Results and discussion

3.1. Surface morphology of pretreated MAO layer

The surface morphology of the MAO coatings obtained after each pretreatment process is shown in Fig. 2(a–f). From the figure it is evident that MAO coating in as-prepared condition (Fig. 2a) exhibits porous and rough morphology. At higher magnifications, the coating (Fig. 2b) shows the distribution of spherical particles over the surface. This could be due to the dissolution, sintering and cooling of the surface during MAO process. It is reported that the formation of micro-pores is mainly due to the sparking discharge and evolution of gas bubbles during the process. It has also been reported that the formation of microcracks around the pores are due to the thermal stresses generated during the rapid solidification of the molten oxide in the electrolyte. The surface morphology of the coating after immersion in the plating solution for 2 min. is shown in the Fig. 2(c and d) respectively. At lower magnification, the coating does not show any change in the morphology (Fig. 2c). At higher magnification (Fig. 2d), the distribution of distinct spherical white particles of about 200 nm are found over the surface.
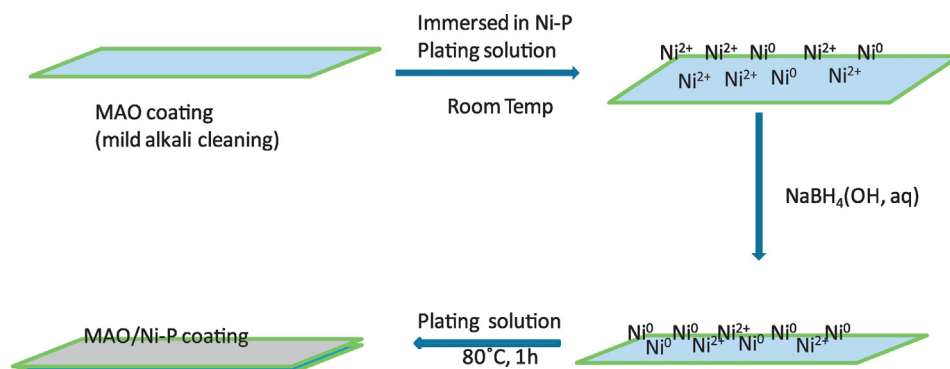

Fig. 1. Illustration of electroless nickel plating on MAO interlayer.