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Study of the structure and corrosion behavior of PEO coatings on AM50 magnesium alloy by electrochemical impedance spectroscopy

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Abstract

In this work coatings were developed on the surface of AM50 magnesium alloy using four different electrolytes containing 10 wt.% each of K_3PO_4 and Na_3PO_4 in combination with either potassium or sodium hydroxides. Electrolyte conductivity and breakdown voltage were measured in order to correlate the property of the coating to the nature of electrolyte. Further, the coatings were examined using scanning electron microscopy for surface morphology and cross sectional investigation, X-ray diffraction for phase determination, and electrochemical impedance spectroscopy for corrosion resistance evaluation. The effect of employing different ions in the electrolytes results in different surface morphologies, chemical phases and, consequently, the corrosion resistance of the coatings. The EIS results indicate the presence of porous and compact layers in the structure of the PEO coatings, whilst the overall coating resistance mainly results from the compact layer, the role of the porous layer as a barrier against corrosion is negligible. Finally, a correlation between the passive current density of the bare alloy and the corrosion resistance of the PEO coating is proposed.

Keywords: Magnesium; Electrolyte; Plasma electrolytic oxidation; Coating; Corrosion

1. Introduction

Growing concern for green house effect and increasing fuel cost have been major driving forces to develop light weight materials for aerospace and automobile applications. Magnesium being the lightest engineering material of all metals remains a potential candidate material for such applications. There has been a surge, in the recent years, in the development of a variety of magnesium alloys that can exhibit high strength and creep resistance. Nevertheless, magnesium and its alloys are prone to corrosion, by virtue of magnesium being one of the most reactive metallic elements, and the oxide it forms, unlike aluminum and titanium, is less protective to the substrate. External protection of magnesium from corrosion is therefore imperative. Various types of protective coatings, namely organic, conversion, ion implantation and plasma electrolytic oxidation (PEO) are suggested for preventing corrosion of magnesium and its alloys [1]. Among these, PEO coatings offer several advantages over other coatings. They provide high hardness, can be used at high temperatures, and the coating process is environmental friendly. These coatings are, however, porous, and require proper selection of electrolytic solutions and of the voltage applied to develop good coatings. Literature concerning the development of PEO coatings on magnesium is sparse as compared to aluminum alloys. Some publications are related to development of PEO coatings on AZ91 [2,3] and AZ31 [4] magnesium alloys. However, corrosion properties of PEO coatings on manganese containing alloys, namely AM-series, have not been much reported. Specific properties of this class of alloys, such as excellent energy absorption and ductility together with reasonable yield and tensile properties make them suitable to be employed for die casting processes to produce parts which require good ductility and toughness such as automotive wheels [5]. It is known that the properties of PEO coatings depend on the nature of the substrate alloy [6]. Hence, it is interesting to develop and study PEO coatings formed on AM50 magnesium alloy. Furthermore, the

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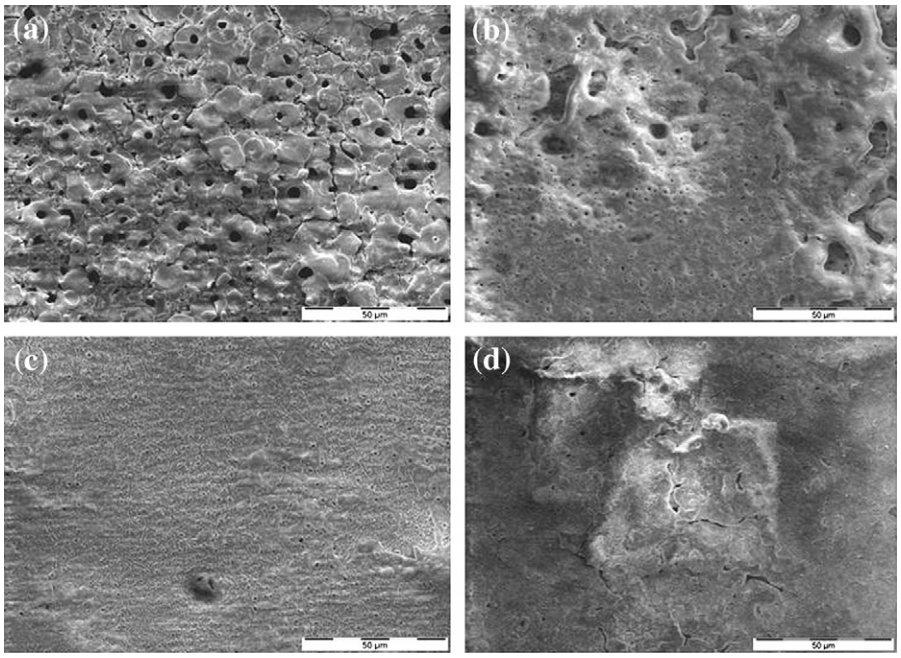

Fig. 1. Surface morphologies of the coating layers produced in (a) K_3PO_4+KOH, (b)Na_3PO_4+KOH, (c) K_3PO_4+NaOH and (d) Na_3PO_4+NaOH electrolytes.

importance of this study lies in the fact that it uses phosphate additives to the electrolyte which are more environmental friendly than using fluorides [7] and chromates [8]. The work also examines the possible effect of cations, namely potassium and sodium, on the morphological and corrosion characteristics of the PEO coatings.

2. Experimental procedure

AM50 magnesium alloy (4.4–5.5 wt.% Al, 0.26–0.6 wt.% Mn, max 0.22 wt.% Zn, max 0.1 wt.% Si, reminder Mg) specimens of 15×15×4 mm size were used as substrates for the coating process. Machined specimens were ground with various grades of silicon carbide papers starting from 800 and reaching down to 2500 grade. In order to get a stable current transfer through the sample to the electrolyte, a threaded hole of 2.5 mm diameter was made on one of the lateral sides of the samples, and such samples were screwed to a holder which also carried the current.

For the PEO process, 10 wt.% KOH and NaOH solutions prepared in distilled water were used. To each of these solutions either K_3PO_4 or Na_3PO_4 salt was added so that the resulting solution contained 10 wt.% of any of these two salts. These combinations led to four different electrolyte formulations.

The used power supply has the capability to produce AC and DC current in ordinary and pulsed form up to 1000 V. The samples were treated under pulsed DC current for a total duration of 5 min at the following conditions: 0.15 A/cm^2 constant current for 2 min, and subsequently the current was reduced and kept constant at 0.075 A/cm^2 for 3 min. During the process, the breakdown (V_{BD}) and final voltages of the PEO process were recorded.

After the coating process, scanning electron microscopy (Cambridge Stereoscan 250) was employed to observe the surface morphology of the coating. The thickness of the coatings was measured using an eddy-current coating thickness measurement gauge (Minitest 2100, Electrophysik, Germany). The thickness data given are the average of at least three different measurements made at different locations. X-ray diffraction (XRD) was performed using a Siemens diffractometer D 5000 operating with Cu K_α radiation.

For corrosion resistance evaluation of the coatings, electrochemical impedance spectroscopy (EIS) technique was employed using 3.5 wt.% sodium chloride with pH of 6.5 as test solution and by setting up the equipment in the frequency range between 0.1 and 10^4 Hz with an amplitude of ±10 mV. The corrosion cell consisted of an Ag/AgCl (3 mol/l KCl) reference electrode, a Pt counter electrode and the specimen to be coated as the working electrode. All EIS data were analyzed using Zview software.

3. Results and discussion

3.1. Coating morphology

Secondary electron images of the four coatings obtained by the scanning electron microscope are shown in Fig. 1. The appearance of pores on the surface of the coating is characteristic of PEO coatings. A comparative evaluation of the coatings indicates that the size of pores in PEO coatings obtained with potassium hydroxide as the base electrolyte is larger than that obtained using sodium hydroxide. The main reason for such a behavior can be attributed to the operating voltage at which these coatings were obtained [3,7,9]. Generally, in potassium hydroxide electrolytes in order to initiate sparks on the alloy surface higher voltages needed to be applied as compared to sodium hydroxide electrolytes. Thus, K_3PO_4+KOH and Na_3PO_4+KOH electrolytes exhibited V_{BD}

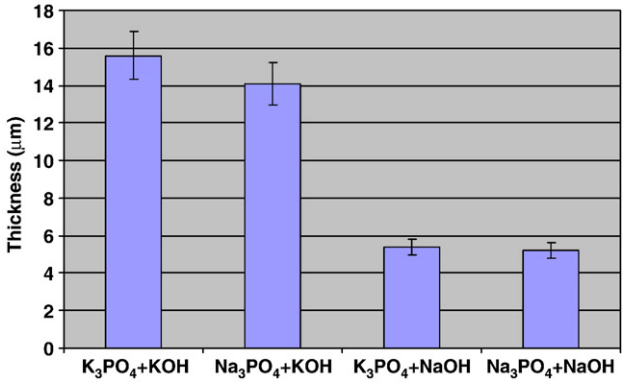

Fig. 2. Variation of thickness of coatings prepared using different electrolytes, measured by an eddy-current thickness measurement gauge.

of 160 and 150 V, respectively, while K_3PO_4+NaOH and Na_3PO_4+NaOH electrolytes exhibited V_{BD} of 116 and 106 V, respectively. Higher voltages promote larger pores within the oxide coating [3,7,9]. A closer observation of PEO coatings obtained in sodium hydroxide as base electrolyte reveals that they exhibit smoother structures, which is not so much evident in PEO coatings obtained in potassium hydroxide electrolytes. The thickness of the coatings measured using the thickness gauge was further confirmed with scanning electron microscope images of the coating cross-section. The variation of the thickness of the coatings obtained in these electrolytes is shown in Fig. 2. It looks as if the alloy formed thicker coatings in those solutions which permitted a higher voltage to be applied during the plasma electrolytic oxidation. Such a behavior is typical of PEO coatings [10,11,12].

3.2. Phase analysis

Typical X-ray diffraction (XRD) patterns obtained on the four different PEO coatings are delineated in Fig. 3. The patterns were analyzed based on JCPDS data. All the XRD patterns revealed the presence of magnesium oxide and magnesium, while only the XRD patterns of the PEO coatings obtained in Na_3PO_4+KOH and Na_3PO_4+NaOH solutions show the existence of an additional phase, namely magnesium phosphate, in the related coatings However, it appears as if the diffracted X-rays corresponding to the magnesium phase arise from the substrate on which the PEO coating was formed. Such an observation has been made by others, who examined PEO coatings and attributed the presence of peaks of magnesium to the X-ray penetration into the substrate. This may at least partly be a consequence of the presence of fine pores in the coating [13].

The fact that a magnesium phosphate phase is not observed in the XRD patterns of PEO coatings obtained in electrolytes with K_3PO_4, irrespective of the nature of the cations present in the base electrolyte, indicates that it was not just the phosphates of the electrolyte that determined the coating characteristics, but also the nature of cations of the phosphates (K_3PO_4/Na_3PO_4) used in the electrolyte formulation. The reason for such an effect on the formation of coatings is not clear.

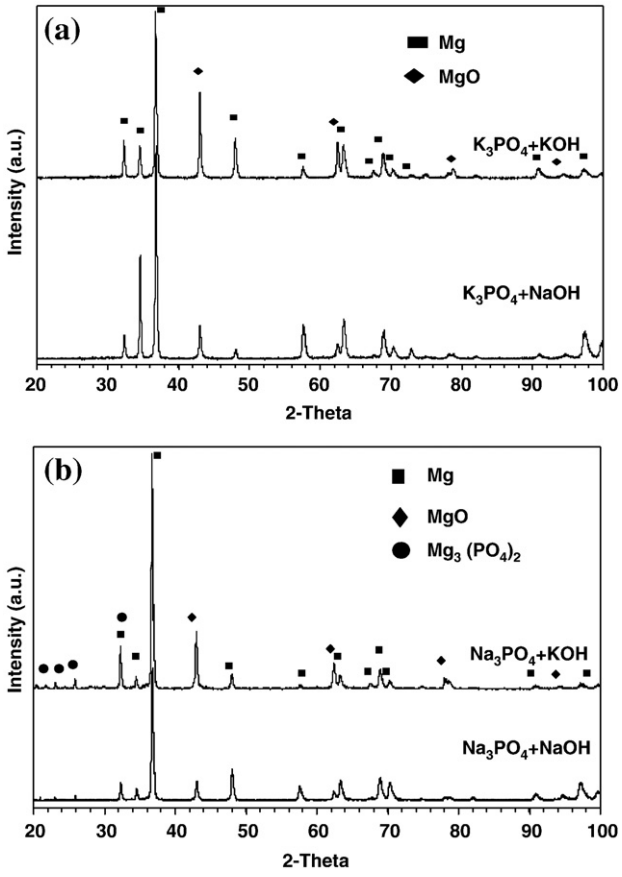

Fig. 3. XRD patterns of coatings: (a) K_3PO_4, (b) Na_3PO_4 electrolytes containing hydroxides.

It is necessary to point out the fact that the calculated lattice parameter of the MgO phase of all the prepared coatings remained almost constant at 4.2 Å, irrespective of the type of electrolyte used in the study. The ratio of the major peak of MgO over Mg, $I_{MgO(200)}/I_{Mg\ (101)}$, was calculated for the XRD patterns obtained in all the four solutions. The values were found to be 0.516, 0.247, 0.162 and 0.154, respectively, for the coatings obtained in K_3PO_4+KOH, Na_3PO_4+KOH, K_3PO_4+NaOH and Na_3PO_4+NaOH solutions. It can clearly be seen that the decrease in the values is in agreement with the measured thickness of these coatings in Fig. 2.

3.3. Electrochemical impedance

Electrochemical impedance spectroscopy was employed to analyze the corrosion characteristics of the four PEO coatings.

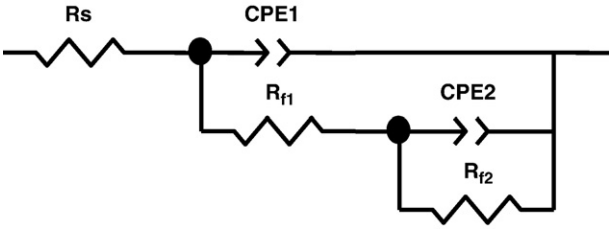

Fig. 4. Equivalent circuit employed to analyze the data.

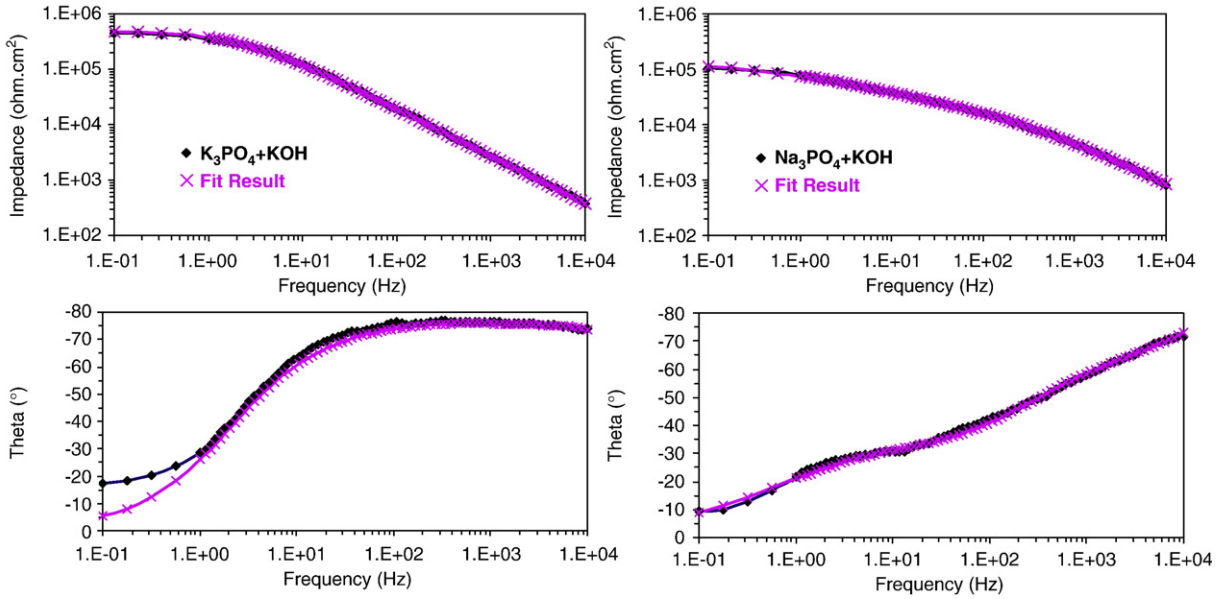

Fig. 5. Fit result of Bode plots relating to the K_3PO_4+KOH and Na_3PO_4+KOH coatings.

Several equivalent circuit models representing different types of electrode/electrolyte interfaces were utilized to simulate the obtained experimental data. However, the most satisfactory data fit with the lowest chi square value and weighted average error was obtained with an electrical equivalent circuit with two time constants as shown in Fig. 4. Attempts to include more elements gave rise to unrealistically large errors for the additional elements. Hence, the experimental data were fitted with this simple equivalent circuit. To get a better fit and also include a surface inhomogeneity factor and a possible diffusional factor, a more general constant phase element (CPE) was used instead of a rigid capacitive element. The capacity element is expressed by the following equation;

$$Z_{\mathrm{CPE}} = 1/\left[T(j\omega)^{P}\right] \tag{1}$$

Where T is CPE constant, j is the imaginary unit $\left(\sqrt{-1}\right)$, ω is the angular frequency (1 rad/s) of the sine wave being considered as $\omega = 2\pi f$, f is the frequency in Hz; the value of P ranges between 0 and 1. The values 0, 0.5 and 1 of P imply the CPE of the circuit to be pure resistor, Warburg impedance and capacitor, respectively.

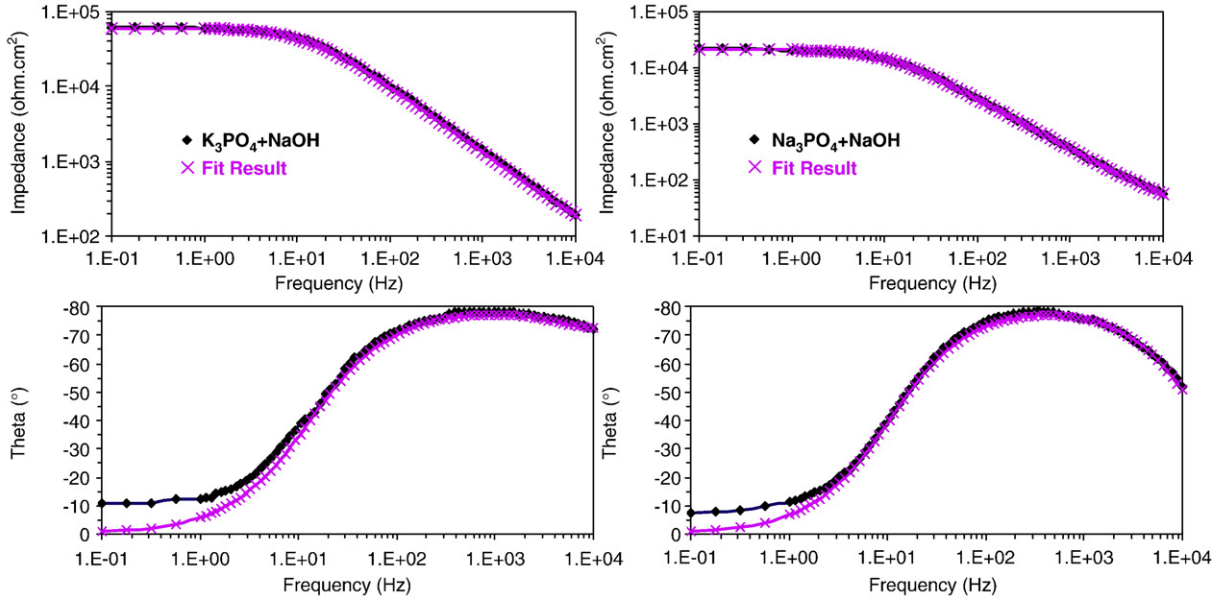

Fig. 6. Fit result of Bode plots relating to the K_3PO_4+NaOH and Na_3PO_4+NaOH coating.

Table 1
Equivalent circuit data

Electrolyte type	CPE1-P	CPE1-T	R_{f1} ($\Omega \cdot cm^2$)	CPE2-P	CPE2-T	R_{f2} ($\Omega \cdot cm^2$)	Chi-squared	Weighted sum of squares
K_3PO_4+KOH	1.000	4.07E-08	1797	0.73	2.55E-07	5.02E05	4.73E-3	0.76
Na_3PO_4+KOH	0.944	3.28E-08	1220	0.41	3.69E-06	1.58E05	1.01E-3	0.16
K_3PO_4+NaOH	0.865	3.35E-07	1173	1.00	1.90E-08	5.99E04	7.27E-3	1.17
Na_3PO_4+NaOH	0.889	1.10E-06	812.2	1.09	1.93E-08	2.03E4	3.35E-3	0.54

The impedance plots shown in Figs. 5 and 6 illustrate a good fitting between the experimental data and the simulated values. The two time constants represented in the equivalent circuit correspond to the porous and the compact coatings. Though Blawert et al. [14] by using different electrolyte reported four types of layers for PEO coatings from a microstructural point of view, it was not possible to fit the data to such a physical model from an electrochemical response point of view. Introducing an additional interface in the proposed equivalent circuit to represent the magnesium alloy/solution interface (double layer and charge transfer resistance) gave rise to an unduly high charge transfer resistance of the order of 1×10^{20} Ω cm^2, with a very large error for this element. The circuit elements calculated from the fitting are summarized in Table 1. The EIS data provide the following information regarding the nature of the coating.

The resistance (R_{f1}) of the outer porous coating is too small compared to that of the compact coating (R_{f2}) and it does not significantly contribute to the corrosion protection of the AM50 alloy substrate. Furthermore, the resistance of the porous coatings (R_{f1}) does not seem to differ significantly from one another, though the scanning electron microscope reveals the surface morphology of coatings to be different. Although the surface layer on the coating obtained in sodium containing electrolyte (electrolyte containing Na_3PO_4 and/or NaOH) seems to be smooth and compact, close examination of the coating obtained in Na_3PO_4+KOH indicates that such an appearance is superficial and that the structure below is quite porous, having large discharge channels, and in the coating obtained in Na_3PO_4+NaOH electrolyte micro cracks within this superficial layer can also be seen.

The resistance of the compact coating R_{f2} obtained in four different solutions increases in the order Na_3PO_4+NaOH < K_3PO_4+NaOH < Na_3PO_4+KOH < K_3PO_4+KOH. Since the resistance of the porous layer (R_{f1}) is insignificant as compared to that of compact layer (R_{f2}), the overall corrosion resistance of the coating depends on the latter. Thus, the thickness of the coating as indicated in Fig. 2 can not be related to the corrosion resistance. However, it must be pointed out that the coating obtained in K_3PO_4+KOH solution is not only the thickest but that it also exhibits the highest resistance among the four coatings. This aspect will be discussed in more detail further below.

Comparing the EIS data of PEO coatings obtained using phosphate solution and reported in the literature for AZ91 and AZ31 alloys [3,4,15,16] with that of AM50 alloy, it can be said that the present coatings exhibit reasonable R_{f2} values and hence these coatings show appropriate corrosion resistance.

4. Discussion

Based on the EIS studies, the plasma electrolytic oxidation coatings obtained with four different electrolytes containing combinations of phosphates and hydroxides of sodium and potassium were found to have a top porous layer followed by a compact layer. The corrosion resistance of the top porous layer (R_{f1}) was found to be insignificant compared to the compact layer and these values do not significantly differ from one coating to another. Thus, the large channels formed in the potassium hydroxide coatings do not significantly alter the corrosion resistance of the coating compared to the smaller holes on the surface of the sodium hydroxide coatings. The resistance of the compact layer, however, is significantly affected by the nature of the electrolyte. The electrolytes with potassium ions in the form of either hydroxide or phosphate solutions or both produce corrosion resistant compact layers. When the solution contains only potassium ions in addition to phosphate ions, it results in the highest resistant of the compact coatings. It should also be pointed out that the voltages at which sparks occur in electrolytes containing potassium ions are higher than those occurring in electrolytes containing sodium.

Published literature regarding the fundamental understanding of the plasma electrolytic oxidation process and coating properties such as corrosion and wear is rare, though the physical and chemical processes occurring during PEO that lead to coating formation have been described by various authors [6,17,18]. One of the important PEO coating process parameters, namely the breakdown voltage, has been widely studied by several authors [4,6,19]. The nature of the metal, the electrolyte composition and the electrolyte conductivity are known to affect the breakdown voltage [6]. The present work is also in agreement with the fact that breakdown voltages of coatings formed with Na_3PO_4+NaOH, K_3PO_4+NaOH, Na_3PO_4+KOH, K_3PO_4+KOH solutions are found to increase with the decrease in the conductivity of these electrolytes. The conductivity of the electrolytes are 52.8, 53.5, 39.8 and 39.9 mS/cm^2,respectively, and the breakdown voltages of coating formation in these electrolytes were found to be 106, 116, 150 and 160 V, respectively.

The breakdown voltage of the PEO coatings affects the porosity of the coating; with an increase in V_{BD}, an increase in the size of the pores is observed. The impedance studies show that these coatings develop very high porosities even at low V_{BD} values, any further increase in porosity due to high V_{BD} value hardly affects the corrosion resistance of the resultant coating.

As per the EIS analysis, the structure of a PEO coating can be described as the one that consists of a compact barrier layer on

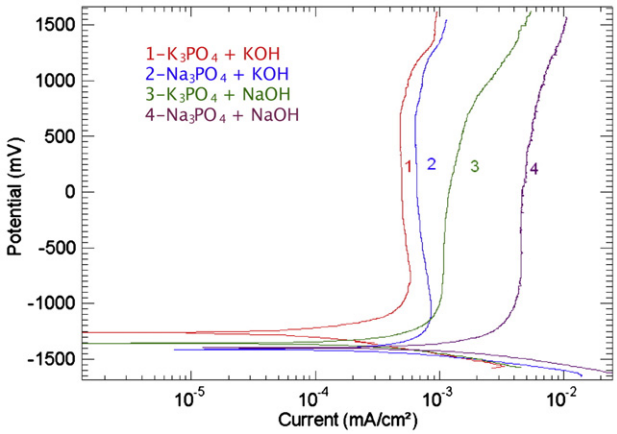

Fig. 7. Anodic polarization of AM50 without coating in the four coating solutions employed; 1—K_3PO_4+KOH, 2—Na_3PO_4+KOH, 3—K_3PO_4+NaOH and 4—Na_3PO_4+NaOH.

the surface of the metal followed by a porous interconnected layer over the compact layer. While the porous layer is formed as a result of plasma interaction with the metal and electrolyte, the barrier layer is formed as a result of the applied potential over the metal. Hence, the electrochemical property of this film depends on the chemistry of the alloy and the environment to which it is exposed [6]. Therefore, an attempt was made to correlate the passivation behavior of the metal in the electrolyte to the corrosion resistance of the PEO coating. Fig. 7 shows the polarization plots of AM50 alloy obtained in the four different electrolytes employed in the present case. Comparison of the passive current density of the plots with the corrosion resistance of the PEO coating (reflected in terms of R_{f2}) indicates that there is a trend with respect to these parameters. As the solution acquires high ability to promote alloy passivity, it also has better tendency to increase R_{f2} of the PEO respective coating. It is also interesting to point out the fact that the breakdown voltage was found to increase with a decrease in the passive current density of the alloy. It is known that the breakdown potential of a passive metal increases with an increase in the passivity of the alloy. From that respect, the passive current density seems to be related to the sparking potential. But, more studies are required in order to substantiate this point.

5. Conclusions

1. It was possible to develop a good corrosion resistant PEO coating on magnesium AM50 alloy, consisting of a compact and a porous layer.
2. The results show that the porous layer of the coating is inconsequential with respect to corrosion, while the corrosion resistance depends on the compact layer of the coating which is in direct contact with the alloy.
3. The nature of cations associated with hydroxide or phosphates present in the electrolyte influence the corrosion resistance of the coating.
4. The corrosion resistance of a PEO coating formed on AM50 alloy is found to be reflected by the passivation current density in the electrolyte in which the PEO coating is formed.

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