Effect of electrolytic solution on corrosion behavior and mechanical properties of a coated AZ31 magnesium alloy via plasma electrolytic oxidation process

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Abstract: The present work deals with the corrosion behavior and mechanical properties of a coted AZ31 magnesium alloy through plasma electrolyte oxidation (PEO) coating process in different alkaline electrolytes based on sodium silicate (Si-coating), sodium polyphosphate (P-coating) and sodium aluminate (Al-coating). The scanning electron microscopy (SEM) equipped with the energy dispersive x-ray spectroscopy (EDX) plus x-ray diffraction were recruited to investigate the morphology, chemical composition, and phase structure of coatings, respectively. Microscopic scrutiny revealed that the coating in the phosphate electrolyte was twice as thick and the relative porosity percentage was higher than those formed in the other electrolytes. The phase analysis indicated that the MgO was present as the prevailing phase in the Al-coating and P-coating. However, the dominant phase in the Si-coating was Mg_2SiO_4. Electrochemical testing was examined in a solution containing 3.5.wt% sodium chloride, showing improvements in corrosion resistance of coated alloys. These investigations confirmed that the corrosion resistance of Si-coating was dramatically higher than others which could be attributed to the presence of the dense and stable Mg_2SiO_4 phase as well as its relatively low porosity. According to the results of tensile tests, the coated samples had lower tensile strength and elongation than the uncoated one. The tensile strength and elongation diminished upon changing the electrolyte from Al-coating to P-coating, while the yield strength was almost similar. Further analyses indicated that the drop of tensile strength and elongation could be attributed to the presence of cracks and pores in the brittle ceramic PEO coating as stress concentration regions during deformation. Those areas are created due to thermal stress during the coating process and deformation in the elastic stage.

Keywords: Mechanical properties; AZ31 Magnesium alloy; plasma electrolytic oxidation (PEO); corrosion behavior.

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Nomenclature	
PEO	Plasma Electrolyte Oxidation
Si-coating	Silicate containing sample
P-coating	Polyphosphate containing sample
Al-coating	Aluminate containing sample
SEM	Scanning Electron Microscopy
PVD	physical vapor deposition
EDX	Energy Dispersive x-ray Spectroscopy
XRD	X-Ray Diffraction
DC	Direct Current
SCE	Saturated Calomel Electrode
FRA	frequency response analyzer
V_{BD}	Breakdown Voltage
a_B	definite constant for the metal
b_B	definite constant for the electrolyte
k	ionic conductivity of the electrolyte
E_P	single pulse energy
U_P	pulse voltage
I_p	pulse current
t_{on}	pulse-on time
OCP	Open Circuit Potential
i_{corr}	corrosion current density
E_{corr}	corrosion potential
β_c	cathodic Tafel slopes
β_a	anodic Tafel slopes
ASTM	American Standard Test Method
R_P	Polarization Resistance
CPE	Constant Phase Element
$C_{CPE,i}$	capacitance values of the constant phase element
$Y_{0,i}$	admittance constant
R_i	parallel resistance to the constant phase element I
n	heterogeneity factor.
YS	Yield Strength
UTS	Ultimate Tensile Strength
ε	Strain

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1. Introduction

Magnesium alloys with special properties such as low density, high specific strength, excellent damping capacity, and good protection against electromagnetic waves have a great potential in engineering applications such as aerospace, automotive, and electronics industries. At the same time, there remains a concern about their poor corrosion resistance due to their high chemical activity and very negative electrochemical potential. The latter severely weakens the mechanical properties by creating stress concentration areas. For this reason, the use of magnesium alloys is limited [1, 2] .

Various surface treatments have been introduced to improve the corrosion properties of magnesium alloys, including conversion coatings [3], electroplating [4], anodizing [5], plasma electrolytic oxidation [6], polymer coatings [7], and physical vapor deposition (PVD) [8]. The plasma electrolytic oxidation (PEO) process is recognized as a relatively new and cost-effective method for modifying the surface of valve metals (aluminum, titanium and magnesium) in environmentally friendly alkaline electrolytes through producing dense, hard, and adhesive ceramic coatings which boosts the corrosion resistance of substrate [9]. To improve the quality of the coating formed on magnesium alloys, knowledge of the mechanisms and parameters affecting the PEO process is essential [10]. Thus, many studies have been undertaken on the ignition mechanism and growth of the coating, as well as parameters affecting the quality of the coating, including electrolyte composition, electrical parameters of the device, and coating time[11-14]. In this regard, by examining the effect of SiO_3^{2-}, PO_4^{3-}, and AlO_2^- anions on the corrosion properties of PEO coating applied to AM50 magnesium alloy, Ghasemi et al. [15] observed that these anions affect the coating characteristics such as thickness, chemical composition, and structure of the coating. They reported that the coating formed in the electrolyte containing SiO_3^{2-} showed more favorable corrosion properties than the two electrolytes due to the thickness, low number of open porosity, and optimal barrier layer resistance. Rahman et al. [16] also evaluated the effect of three additives of phosphate, silicate, and aluminate to electrolytes containing NaOH and Na_2SiF_6 on the structure and tribological characteristics of the coating. The results of this study revealed that the coating formed in the electrolyte containing alumina had better hardness and tribological properties.

In general, to improve the corrosion resistance of magnesium, various processes are used to prevent the loss of mechanical properties of the alloy. For example, extensive research has been done to explore the effect of plasma electrolytic oxidation treatment on the mechanical properties while specimen have exposed to a corrosive environment, like stress corrosion cracking behavior of magnesium alloy[17-19].

But the important question that remains is what effect do such corrosion resistance-enhancing processes alone have on mechanical properties?

So far, no review has been performed on the effect of PEO process before exposure to corrosive atmosphere on these alloys. This study helps in determining the effect of the coating process on the possible attenuation or strengthening of mechanical properties before the corrosion process takes effect to realize whether the sample has adequate conditions for use in the relevant industry.

The present study characterizes the corrosion behavior of oxide coatings created by plasma electrolytic oxidation (PEO) method on the AZ31 magnesium alloy in three different electrolytes of sodium polyphosphate, sodium silicate, and sodium aluminate. Then, the effect of this process was explored on improving the mechanical properties of alloys.

2. Materials and Methods

2.1 .Preparation *of Specimens, Electrolyte Solutions, and PEO treatment*

A wrought magnesium alloy of grade AZ31 with a nominal composition in **Table 1** was employed in this investigation.

Table 1. The chemical composition of AZ31 magnesium alloy.

Elements	Al	Zn	Mn	Si	Cu	Ni	Fe	Other	Mg
(wt.%)	2.5-3.5	0.6-1.4	0.2-1.0	0.1	0.04	0.005	0.005	0.3	Balance

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Specimens of 26 mm × 26 mm × 5 mm were ground successively with 600, 800, 1000, and 2500 grit emery sheets and washed in acetone prior to the PEO treatment. The PEO process was carried out using a pulsed DC power source with a bipolar pulse of t_{on}:t_{off} = 55:15 (1000 Hz). This gradient pulse was repeated with a frequency of 1000 Hz. During the PEO process, a constant current setting was employed by a square pulse and anodic/cathodic pick ratio ($I_+/I_- = 1$) for 5 min. This wave was applied to magnesium alloy for 5 min at room temperature. AZ31 alloy specimens and stainless-steel plates, placed around the cell, were used as the anode and cathode, respectively. As reported in **Table 2**, the three electrolytes were prepared separately whereby distilled water was used as a solvent.

Table 2. Electrolyte composition and coating process parameter.

Samples	Electrolyte composition (g/L)	Flow density $(\frac{A}{cm^2})$	t_+/t_-	Frequency (Hz)
P-coating	10 g/L $Na(PO_3)_n$ + 4 g/L KOH	0.2	$\frac{55}{15}$	1000
Si-coating	10 g/L Na_2SiO_3 + 4 g/L KOH			
Al-coating	10 g/L $NaAlO_2$ + 4 g/L KOH			

The electrolyte was continuously stirred by a magnetic stirrer during coating. The electrolyte temperature was kept constant at 23°C using a heat exchanger system. The potential discrepancies between the anode and the cathode were recorded instantly by a multimeter equipped with a Ziegler RM-232 data recorder. Finally, the coated samples were rinsed with deionized water and dried in warm air.

2.2 .Characterization, Electrochemical, and Tribological Evaluations

The surface morphologies, thickness, and chemical composition of the PEO-AZ31 alloys were characterized using scanning electron microscopy (Cam Scan-MV2300). For cross-sectional analysis of the PEO-AZ31 alloys, the alloys were mechanically cut in half using a wire cut. Cross-sections were prepared through hand polishing with 600–1200 grit SiC paper successively. All samples were coated with a thin coating of gold/palladium using a sputter coater (Bio-Rad® E5400) to improve conductivity and imaging using SEM. Elemental mapping was performed using EDX (Bruker AXS5350, Germany). The porosity and coating thickness measurements were performed based on at least three SEM micrographs of each sample and with the help of MIP plus Processing Lab image analysis software.

The XRD measurements were performed using a commercial X-ray diffractometer (Philips Xpert, λ = 1.5406 A, 40 mA, 40 kV). The scanning range of diffraction angle (2θ) was set between 10° and 100° with steps of 0.02° and time step of 1 s. Due to the low thickness of the coating as well as its high porosity, the coatings were pulverized after which X-ray diffraction test was taken from them.

The electrochemical measurements were made on bare and PEO-coated AZ31 magnesium samples in 3.5 wt.% NaCl solution using a three-electrode system including magnesium specimen as working electrode, a graphite mesh as auxiliary electrode, and calomel electrode as reference electrode. Potentiodynamic polarization test was carried out from the potential of -0.4V (vs. OCP) to 1V SCE with a scan rate of 1 mV.s-1. Electrochemical impedance spectroscopy (EIS) test was conducted on these specimens using a Potentiostat/Galvanostat (Solartron 1260 model) coupled with the frequency response analyzer (FRA) at open circuit potential (OCP) in 3.5 wt.% NaCl electrolyte solution after 60 minutes of immersion at 25 ℃ along with sinusoidal perturbation equal to 5 mV from 100 kHz to 10 mHz frequency range. The impedance spectra were analyzed by ZsimpWin software.

The mechanical properties of the experimental alloy and processed materials were evaluated using tensile testing method. The tensile specimens were prepared according to the E8 standard with 20-mm gauge length, 3-mm gauge width, and 1-mm thickness. The room temperature tensile tests were carried out utilizing a STM50 testing machine with strain rate of 10^{-4} s^{-1}.

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3. Results and discussion

3.1 Voltage-time response curve of PEO prosses

Fig. 1 displays the voltage-time curve of the PEO process in base electrolytes of silicate, phosphate, and aluminate for 300 seconds. The samples were coated at constant current density, consisting of two parts, ion current and electric current density [20].

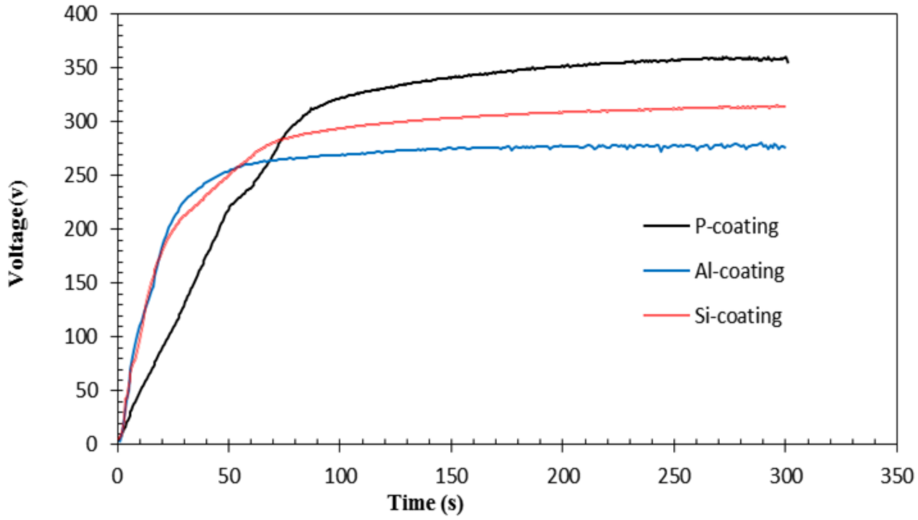

Fig. 1. Voltage-Time response curves of the PEO coated samples.

These curves show three steps for all samples. In the first stage, the dissolution of the metal due to applying a voltage was accompanied by the formation of a thin layer of oxide followed by the release of oxygen gas due to the normal anodizing process. At this stage, the ionic fraction of the current density was dominant and as a result the voltage values increased due to the increase of ionic resistance because of the growth rate of the oxide film [20]. In the second stage, once the voltage reached a critical value (D-electric breakdown voltage), the voltage growth rate diminished and continued until a stable voltage was reached, which can be attributed to both ionic and electrical parts of the current density [21]. This stage began with tiny blue or white sparks followed by yellow micro-sparks caused by micro-discharges. During the third stage, after reaching a stable voltage, the micro-sparks were enlarged, the life of the micro-sparks increased, while the number of sparks decreased. The breakdown voltage, the stabilization voltage and conductivity of electrolyte for the Si-coating, Al-coating, and P-coating were summarized in Table 3. As can be seen D-electric breakdown voltage and stability voltage are strongly dependent on the ion composition and conductivity of the electrolyte [22].

Table 3. Process parameters in different electrolytes.

Samples	Conductivity of electrolyte (mS/cm)	V_{BD}	V_s
P-coating	14.7	220	360
Si-coating	18.3	185	315
Al-coating	21.5	180	280

The relationship between the breakdown voltage and the ion conductivity of the electrolyte is expressed through the theoretical model proposed in **Eq. (1)** by Ikonopisov [23]:

$$V_{BD} = a_B + b_B \log\frac{1}{k} \qquad (1)$$

Where, V_{BD} represents the breakdown voltage, α_B denotes a definite constant for the metal, b_B is a definite constant for the electrolyte, and k shows the ionic conductivity of the electrolyte.

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Considering the inverse relationship between the breakdown voltage and the ionic conductivity of the electrolyte, it can be concluded that the reduction of the ionic conductivity of the electrolytes from Si-coating, Al-coating, and P-coating, respectively increased the breakdown voltage of their respective coatings.

3.2.Morphology and chemical composition of coating

Surface morphology and image analysis of porosity of coatings are shown in **Fig. 2**.

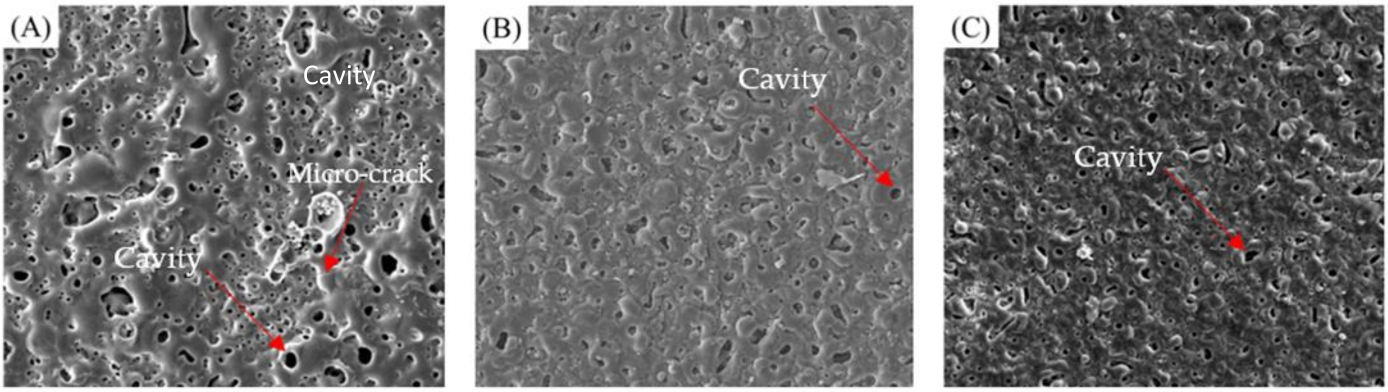

Fig. 2. Surface morphology and image analysis of porosity (A) P-coating, (B) Si-coating, (C) Al-coating.

Surface porosity is visible in all three coatings. Cavities and micro-cracks on the surface are caused by the release of oxygen gas and oxide melting due to the electrolysis process, local plasma temperature and pressure; and thermal stresses due to cooling of the oxide melt, respectively [24]. Researchers have argued that coating time and current density determine the quality of coating [25, 26]. Meanwhile, the results of image analysis of porosities (**Table 4**) reveal that at the equal coating time and current density for different electrolytes, with increasing stability and breakdown voltages of the coating process, the percentage of porosity and diameter of cavities has increased.

Table 4. Average pore diameter and porosity percentage for different electrolytes.

Samples	Average pore diameter (μm) ± 0.1	Porosity percentage (%) ± 0.2
P-coating	1.5	5.7
Si-coating	1.3	4.3
Al-coating	0.7	3.6

Eq. (2) indicates the relationship between voltage and single pulse energy (E_P):

$$E_P = \int_0^{t_{on}} U_p \, . \, I_p dt \tag{2}$$

Where, U_P is the pulse voltage, Ip denotes the pulse current, and t_{on} is the pulse-on time. According to this equation, as the voltage increases, so does the single pulse energy; thus, the morphological characteristics and growth rate of the coating are affected by the voltage and micro-discharge characteristics [27]. On the other hand, the breakdown voltage and other electrical characteristics of the process depend on the electrolyte composition.

Fig. 3 depicts the SEM micrograph and the distribution map of the elements at the cross-section of the samples.

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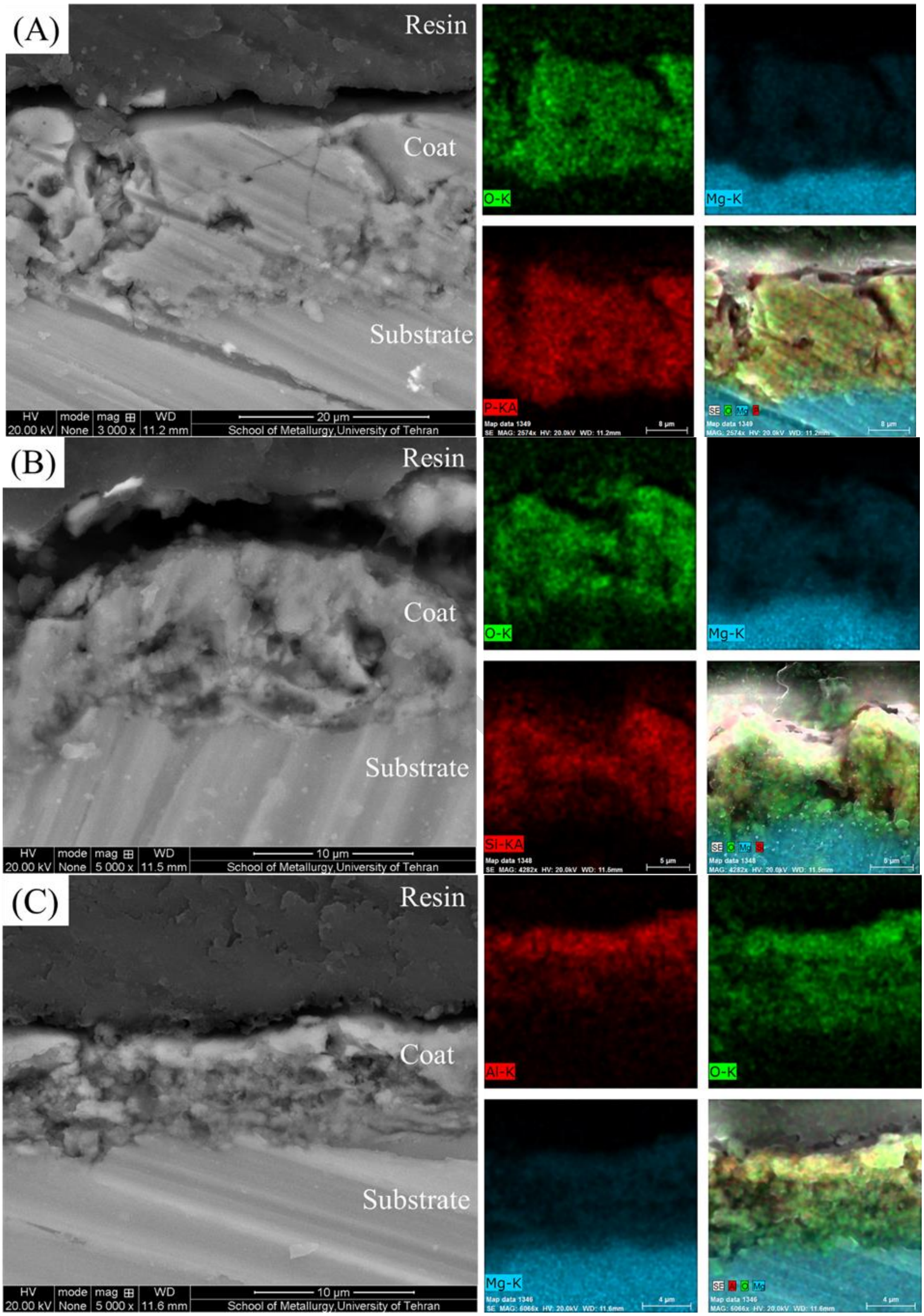

Fig. 3. Cross section SEM micrographs and elemental distribution map of (a) P-coating, (b) Si-coating, (c) Al-coating.

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The thickness of PEO coatings depends on the electrical parameters and the time of the coating process [28]. Given that the current density and the time of coating had constant values, the thickness of the coatings had to be approximately equal; however, the stability voltage and consequently the pulse energy were changed in different electrolytes. According to the values of the stability voltage reported in Table 3, it was expected P-coating and Al-coating to have the highest thickness and the lowest thickness, respectively, which can be seen in Fig. 3 and Table 5. In coating growth rate calculations, the time to reach the breakdown voltage has been considered as the beginning of the coating growth phase.

Table 5. Average coating thickness for coatings produced in three different electrolytes

Samples	Average coating thickness (μm) ± 0.1	Coating growth rate (μm/min)
P-coating	19.6	4.9
Si-coating	12.2	2.6
Al-coating	7.3	1.6

The elemental distribution map of P-coating clearly shows the presence of large cavities caused by large PEO sparks that have reached from the surface to near interface of the coating and the substrate. For Si-coating, there are some holes in the middle of the coating. The elemental distribution map of the Al-coating, despite its uniformity in growth, reveals discontinuities and low compression in the inner part of the coating. As can be seen in the Al element distribution map for the Al-coating, only on the surface of the coating, more stable compounds with suitable compaction of aluminate anions and substrate metal cations are formed.

3.3.Phase composition of coating

Fig. 4 demonstrates the XRD pattern of Si-coating, P-coating, and Al-coating.

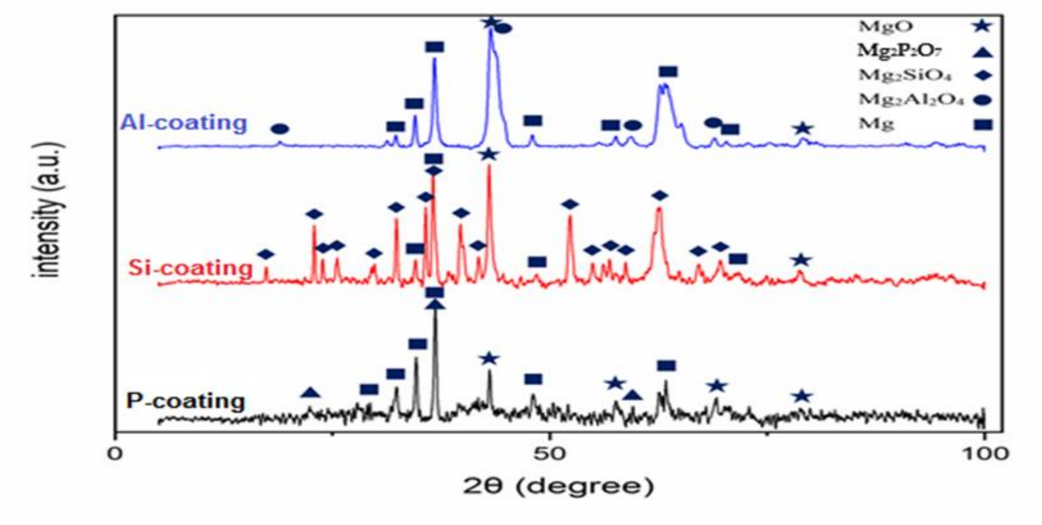

Fig. 4. XRD patterns for PEO coated samples.

Phase composition, the thickness, and porosity of the coating are the effective parameters on the corrosion resistance performance of PEO coatings [5, 29]. The MgO and Mg phases are observed in the pattern of all three samples. The presence of Mg peak in the pattern of the samples is due to chips being removed from the substrate during scraping of coating. In addition to MgO phase, $Mg_2P_2O_7$, Mg_2SiO_4, and $MgAl_2O_4$ phases were also identified in the pattern according to the type of electrolyte. The MgO phase has been predominant in P-coating and Al-coating, while the Mg_2SiO_4 phase has been predominant in the Si-coating.

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The components of the electrolytes produce such as Na_2SiO_3, $Na(PO_3)_n$ and ionized $NaAlO_2$; and OH^- ,O^{2-}, PO_3^-, SiO_3^{2-} and AlO_2^{2-} anions through plasma electrolysis of the electrolyte at high voltages. Mg^{2+} cations are produced from the substrate atoms through discharge channels. The cation Mg^{2+} moves outwards while the mentioned anions move inwards in the path of the discharge channels to form a coating due to the strong electric field caused by the plasma, through performing chemical reactions:
Magnesium anodic dissolution reaction:

$$Mg \longrightarrow Mg^{2+} + 2e^- \tag{3}$$

MgO formation reaction due to dehydration of $Mg(OH)_2$ using high temperature plasma [30]:

$$Mg^{2+} + 2OH^- \longrightarrow Mg(OH)_2 \longrightarrow MgO + H_2O \tag{4}$$

Mg_2SiO_4 phase formation reactions at high temperature plasma [31, 32] and formation chemical reaction of that in the Si-coating [33]:

$$SiO_3^{2-} \longrightarrow SiO_2 + 1/2\ O_2 + 2e^- \tag{5}$$

$$2\ MgO + SiO_2 \longrightarrow Mg_2SiO_4 \tag{6}$$

$$2\ Mg^{2+} + 2\ SiO_3^{2-} \longrightarrow Mg_2SiO_4 + SiO_2 \tag{7}$$

The reaction of formation of $Mg_2P_2O_7$ phase in the P-coating:

$$2MgO + 2H_2PO_4^- + 2H^+ \longrightarrow Mg_2P_2O_7 + 3H_2O \tag{8}$$

The reaction of formation of $MgAl_2O_4$ phase in the Al-coating [2]:

$$AlO_2^- + 2H_2O \longrightarrow Al(OH)_4^- \tag{9}$$

$$4\ Al(OH)_4^- - 4e^- \longrightarrow 4\ Al(OH)_3 + 2\ H_2O + O_2 \tag{10}$$

$$2\ Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O \tag{11}$$

$$Mg^{2+} + 2Al(OH)_4^- \longrightarrow MgAl_2O_4 + 4\ H_2O \tag{12}$$

$$Al_2O_3 + MgO \longrightarrow MgAl_2O_4 \tag{13}$$

$$Mg^{2+} + Al_2O_3 + 2OH^- \longrightarrow MgAl_2O_4 + H_2O \tag{14}$$

$$AlO_2^- + Mg^{2+} \longrightarrow MgAl_2O_4 \tag{15}$$

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3.4.Corrosion behavior

The corrosion behavior of the coatings was evaluated through polarization and electrochemical impedance methods compared to open circuit potential after one hour of immersion in 3.5 wt. % NaCl solution. Fig. 5 reveals open circuit potential changes over time. The choice of one hour immersion time for the samples was to ensure that the coatings would reach stable electrochemical conditions.

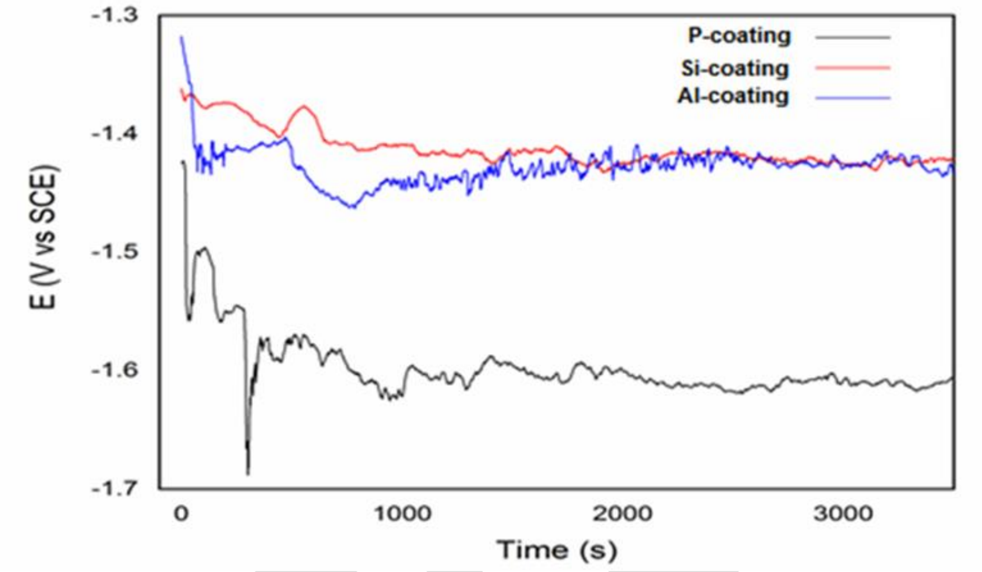

Fig. 5. Variation of open circuit potential (OCP) with time of PEO coated.

Fig. 6 illustrates the Potentiodynamic polarization curves of samples coated in different electrolytes.

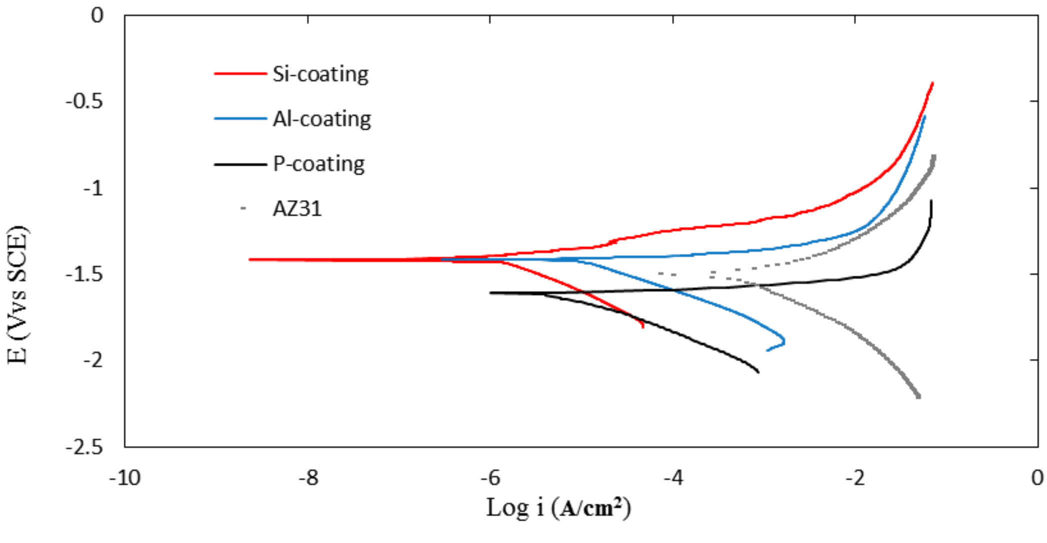

Fig. 6. Potentiodynamic polarization curves of PEO coated and bare Mg alloys at a scan rate of 0.25 mV/s in 3.5 wt.% NaCl solution.

The apparent similarity of the curve of the coated samples can be related to the oxidative nature of the coatings; however, differences in test parameters such as corrosion current density (i_{corr}), corrosion potential (E_{corr}), as well as cathodic (β_c) and anodic (β_a) Tafel slopes can be attributed to differences in surface morphology and fuzzy compositions of the coatings. These parameters were extracted from potentiodynamic polarization curves using ASTM G3 standard and the Tafel extrapolation method. The two

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Tafel branches intersection clarifies the corrosion procedure .The corrosion potential (E_{corr}) is associated with thermodynamic aspect, showing the corrosion susceptibility, while the corrosion current density (i_{corr}) clarifies the corrosion average rate through the area of sampled surface[34]. The values of polarization resistance were also calculated by the Stern-Geary [35] relationship (Eq.16) and presented in Table 6.

$$R_p = \frac{\beta_\alpha \cdot |\beta_c|}{(2.303 I_{Corr}(\beta_\alpha + |\beta_c|))} \qquad (16)$$

Table 6. Summary of DC polarization results for AZ31 substrate and PEO coated samples.

Samples	I_{corr} $1*10^{-6} \pm$ (A/cm^2)	E_{corr} (V)	β_C (V/dec)	β_α (V/dec)	R_p (k$\Omega.cm^2$)
P-coating	9.8	-1.63	-0.14	0.05	3.2
Si-coating	1.1	-1.41	-0.19	0.07	43.8
Al-coating	27	-1.42	-0.17	0.02	1
AZ31	445	-1.52	-0.23	0.12	0.3

In general, a lower i_{corr}, a higher R_p, and a higher E_{corr} normally show a higher corrosion resistance and also a better coating corrosion resistance function[34, 36]. The resistance polarization of Al-coating, Si-coating, and P-coating increased by 3, 146, and 10 times compared to the reference sample (AZ31), respectively. The thickness and porosity are the two main factors affecting the corrosion resistance of coatings [37]. Al- coating has low corrosion resistance despite low surface porosity. As can be seen from the microscopic image and the elemental distribution map, the inner magnesium oxide layer cannot provide high corrosion resistance due to the low Pilling-Bedworth ratio (0.81) as well as the poor quality of the inner coating layer in terms of continuity. Despite the higher thickness of the P-coating than other samples, the high surface porosity and large pore diameter cause corrosive electrolyte penetration paths to the metal surface of the substrate; thus, the corrosion resistance of P-coating is lower than that of the Si-coating.

Fig.7 shows the correlation between the i_{corr} values of coated samples and electrical process characteristics, and morphological characteristics [38]. As can be seen from Fig. 7, the corrosion rate of coatings has no clear relationship with the morphological characteristics and variable electrical parameters of the coating process. Instead, the morphological characteristics of the coating are directly related to the stability voltage and the breakdown voltage and inversely related to the electrical conductivity of the electrolyte. It can also be concluded that the corrosion behavior of coatings does not depend only on the morphological quality of the coating and may also be related to another parameter. The phenomenon that causes a significant difference in the corrosion resistance of the Si-coating to the other two coatings was probably related to two other factors. The first was the difference in the dominant phase formed Si-coating with the dominant phase in the other two coatings, and the second was the difference in the quality of the inner layer of the coating, which can be better investigated by EIS. In Si-coating, according to the XRD results, spinel frostite phase (Mg_2SiO_4) was formed, which according to previous studies was much more compact and stable than the magnesium oxide phase (MgO) formed in the other two samples[5, 15-18, 20-33, 35, 37, 39].

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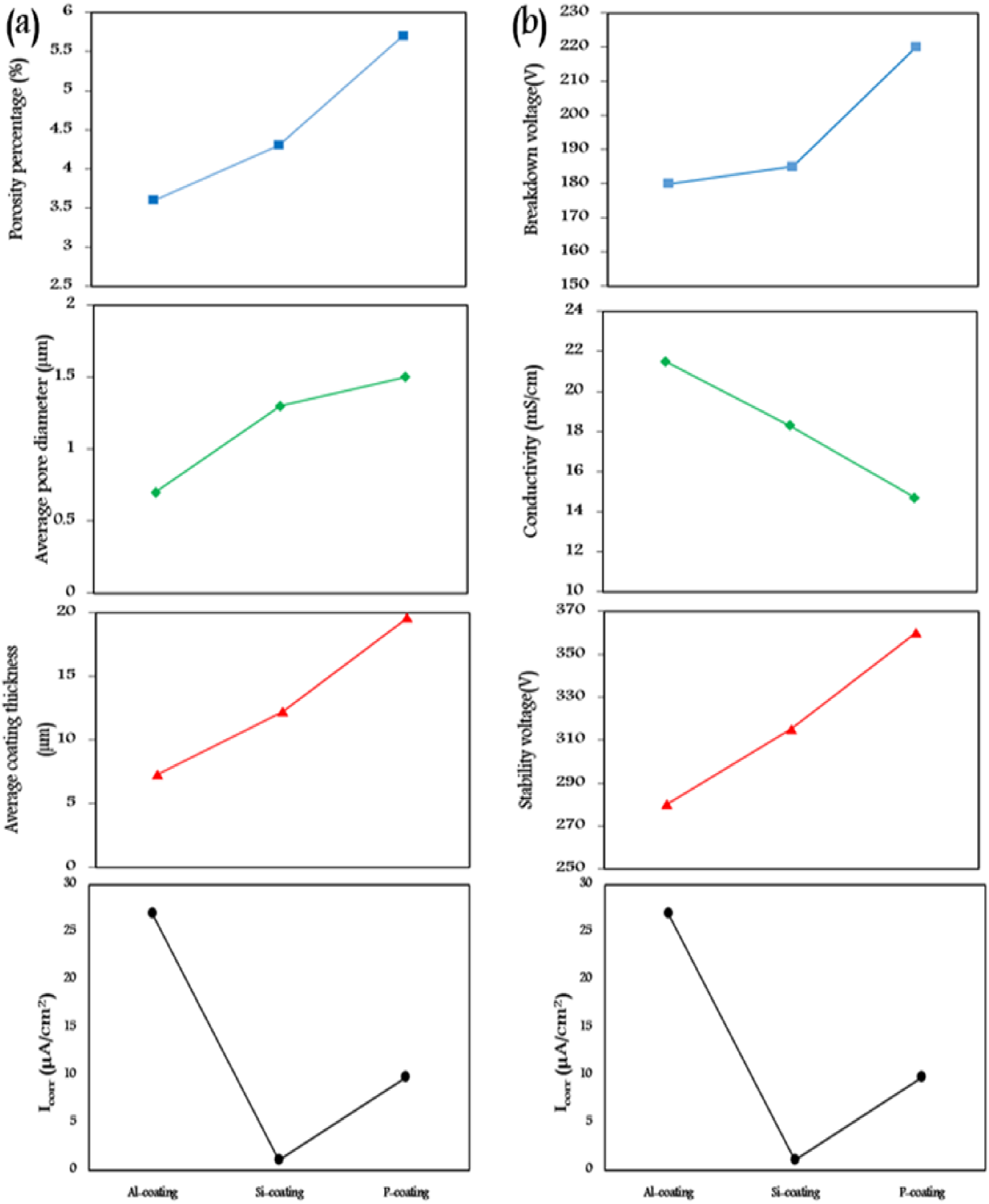

Fig.7. Correlation of icorr with Morphological characteristics (a), electrical process characteristics (b) measured for coatings.

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Fig. 8 and Fig. 9 display the Nyquist and the bode-phase curves of the P-coating, Si-coating, Al-coating, and AZ31 samples, respectively.

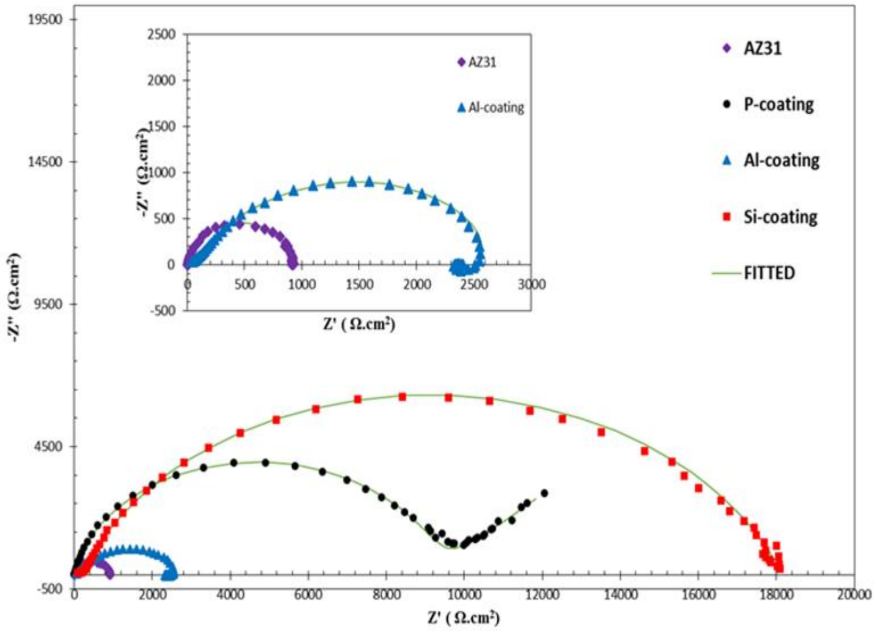

Fig. 8. Nyquist plots of the PEO coated samples and bare Mg alloy.

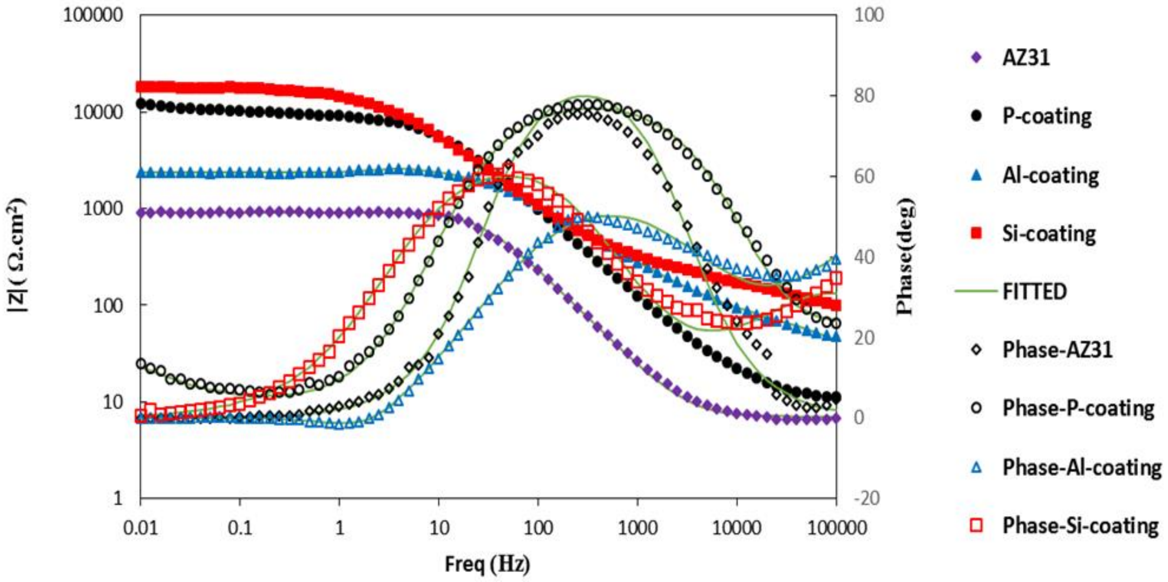

Fig. 9. Bode-Phase plots of the PEO coated and bare Mg alloys.

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The impedance modulus obtained from the low-frequency bode spectra, which is equivalent to the DC (polarization) test conditions, shows that the Si-coating with 18 kΩ.$\boldsymbol{cm^2}$ Polarization resistance offers the best corrosion behavior compared to the P-coating, Al-coating, and AZ31 sample with 9.1, 2.4, and 0.9 kΩ.$\boldsymbol{cm^2}$ Polarization resistances, which is also consistent with the results of potentiodynamic polarization curves.

The Nyquist and Bode-Phase plots of the AZ31 sample indicate that its equivalent circle (Fig. 10a) has a time constant corresponding to the electrolyte / substrate interface.

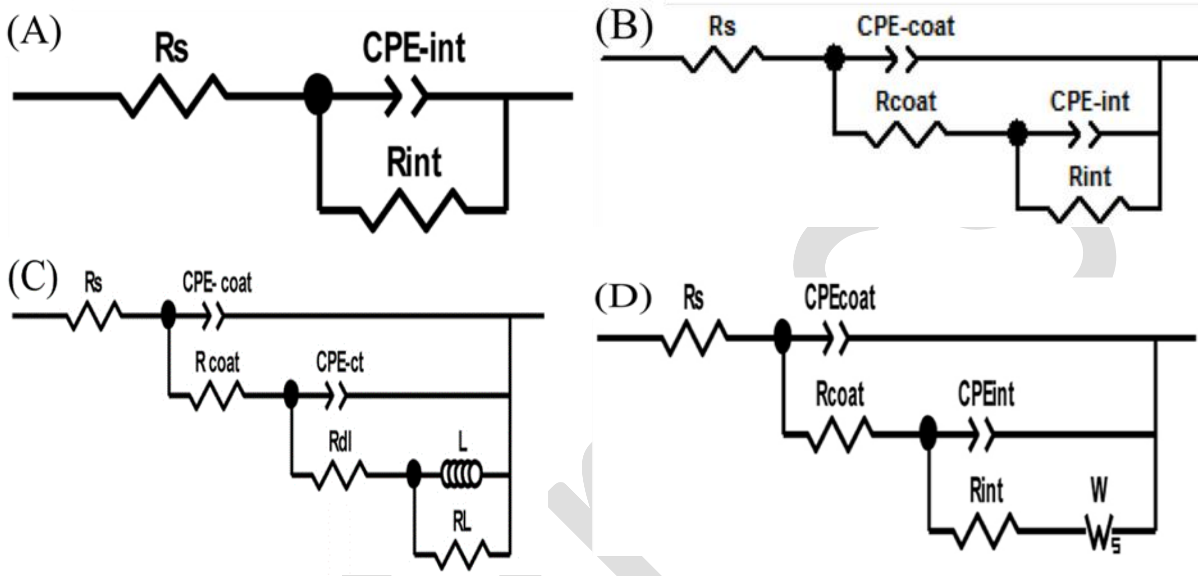

Fig. 10. Equivalent electrical circuits used for impedance data fitting

The impedance spectra of Si-coating reveal two-time constants due to the two-layer coating structure; thus, the equivalent electrical circle (Fig. 10b) has also two time constants (RC). The low frequency time constant is related to the inner compact layer while the high frequency time constant is related to the PEO coating [40]. A negative induction loop can be seen at the lower frequencies of the Nyquist curve of the Al-coating, which corresponds to an inductor element (L) and an inductive resistor (RL) in the equivalent circle (Fig. 10c). This induction loop can be attributed to the reactions of metal dissolution and formation of corrosion products $Mg(OH)_2$ followed by adsorption of electrolyte ion species. These processes lead to the cavity type of localized corrosion on the surface [41]. The impedance spectrum of the P-coating fits well with the equivalent circle to Fig. 10d. The Nyquist and Bode- Phase curves of the P-coating indicate that in addition to two-time constants available for the Si-coating, a Warburg element is also present. The presence of the Warburg element in the impedance spectrum suggests that the process of diffusion control occurs in the coating. Since the P-coating has a high corrosion rate, in order to stabilize the dissolution rate of the substrate, rapid penetration of the invading electrolyte into the porous coating / substrate interface is required, which is called corrosion permeation control [15]. In the equivalent circles (Fig. 10), the constant phase element (CPE) are used (instead of using an absolute capacitor) to capture the surface heterogeneity factor, whereby the obtained results are more accurate by equating the spectra with the electrical equivalent circuit. The capacitance values of the constant phase element are calculated through Eq. 17 [42].

$$\boldsymbol{C_{CPE,i} = (Y_{0,i}.R_i^{1-n})^{\frac{1}{n}}} \qquad (17)$$

Where, $Y_{0,i}$ denotes the admittance constant, R_i represents the parallel resistance to the constant phase element i, and n is the heterogeneity factor. The values of n lie within the range of 0 and 1, indicating that the CPE is absolute resistance (n = 0) and capacitor (n = 1), respectively. The results of equating the impedance spectra of the samples with the equivalent electrical circuits are presented in Fig.10 and Table 7.

Table 7. Various electrical parameter values obtained after equivalent circuit fitting of the EIS data.

Samples	L (H)	R_L (kΩ.cm^2)	W (Y_0)	R_{int} (kΩ.cm^2)	CPE_{int}		R_{coat} (kΩ.cm^2)	CPE_{coat}		R_s (kΩ.cm^2)	Error of fitting (%)
					$Y_{0\text{-}int}$ (Ω^{-1}.cm^{-2}.s^n)	N_{int}		Y_{coat} (Ω^{-1}.cm^{-2}.s^n)	N_{coat}		
P-coating	-	-	$5.7 * 10^{-4}$	8.9	$4.4*10^{-6}$	0.89	0.01	$3.3*10^{-6}$	0.91	0.03	<4.119
Al-coating	50.06	0.9	-	1.2	$6.1*10^{-6}$	0.7	0.31	$1.4*10^{-6}$	0.57	0.03	<5.621
Si-coating	-	-	-	17.9	$2.4*10^{-6}$	0.81	0.22	$1.7*10^{-6}$	0.67	0.03	<6.427
AZ31	-	-	-	0.9	$1.1*10^{-5}$	0.96	-	-	-	0.03	<5.173

The values of R_{coat} and R_{int} of the coatings confirm the fact that the porous layer of the coating cannot provide significant corrosion resistance and the overall corrosion resistance of the coating is mainly related to the compacted inner layer. The corrosion resistance of the porous layer (R_{coat}) of the coating is the lowest for the P-coating and the highest for the Al-coating; thus, the resistance of R_{coat} is inversely associated with the degree of porosity of the coating. R_{int} for Si-coating is equal to 17.9 kΩ.$\boldsymbol{cm^2}$ which is higher than for other samples, which can be due to the presence of a stable forsterite phase in the coating structure, while R_{int} is equal to 1.2 kΩ.$\boldsymbol{cm^2}$ for the Al-coating. The physical concept of CPE parameters (n, Y) can justify the dielectric behavior of the electrolyte / coating interface and the interface of the inner layer /the outer layer[19]. High Y values in the Si-coating may indicate a high corrosive electrolyte contact level at the interface of the inner layer /the outer layer. On the other hand, the low values of n for this sample can be due to the heterogeneity of the contact surface of the corrosive electrolyte and the coating in their interface. Therefore, it can be concluded that the high value of corrosion resistance of the inner layer of Si-coating is due to the high compactness of the phase formed in this coating because the coating has heterogeneous (probably micro-channels that extend from the coating surface to the substrate) that allow penetration of the corrosive electrolyte into the coating.

3.5.Mechanical properties

Fig. 11 depicts the engineering tensile stress vs. strain curves of the samples which exhibit a significant difference.

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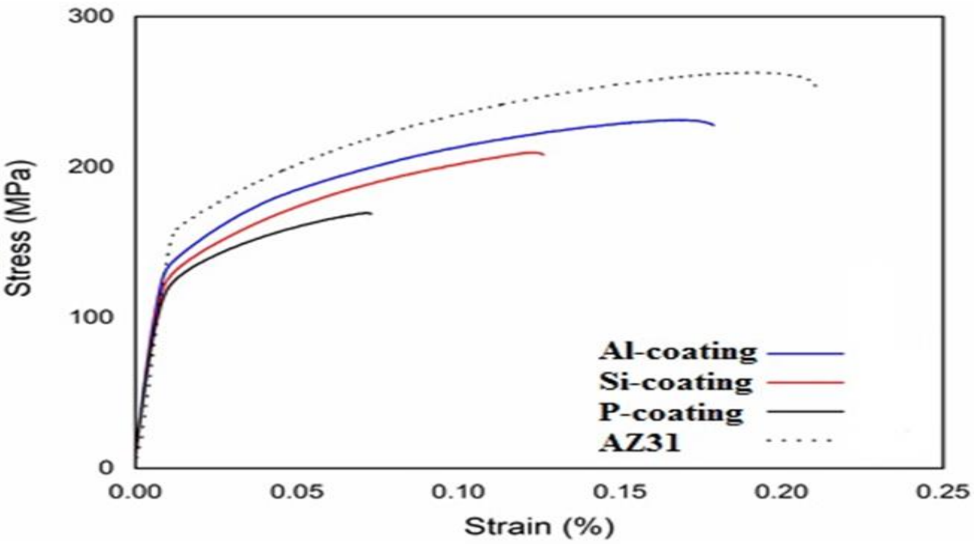

Fig. 11. Stress vs. strain plots of the untreated and PEO-coated AZ31 alloy specimens in air.

The continuously increasing behavior of curves was driven by two different reasons. Elastic and plastic deformation are present in a tensile test as two general deformation stages. Thus, the information regarding the yield strength (YS) as well as the data associated with plastic deformation (ultimate tensile strength (UTS) and strain (ε)) could be derived from the tensile curves. For the uncoated sample, the Hook's law has been ruled in the elastic region, so the tensile stress increased linearly and the yielding stress (YS) has been ~150 MPa at the end of this region. These values have been approximately equal to 133 MPa, 127 MPa, and 120 MPa for Al-coating, Si-coating, and P-coating, respectively (**Fig. 12**).

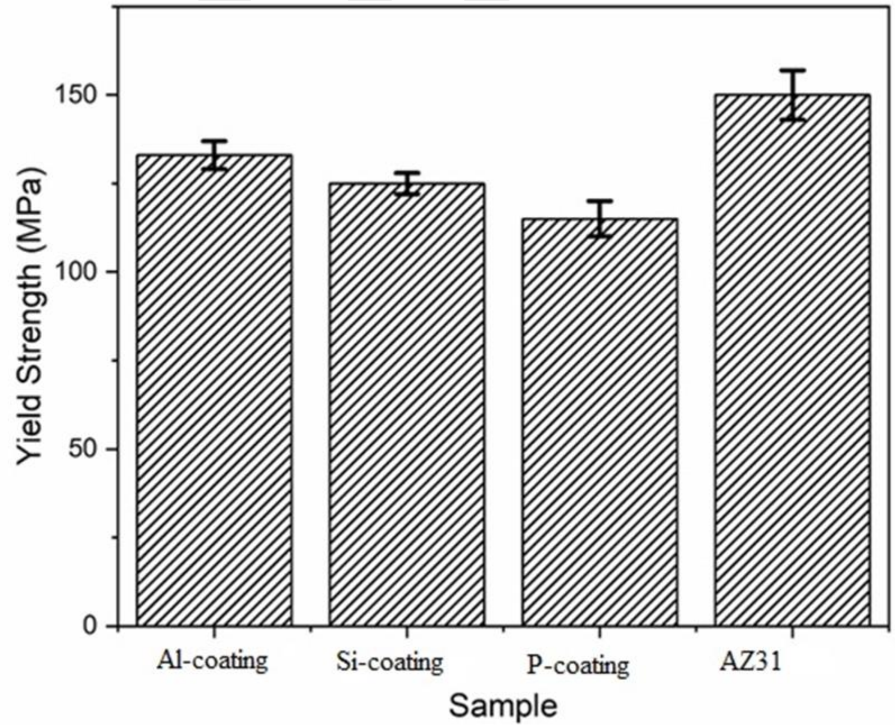

Fig. 12. Yield stress of the untreated and PEO-coated AZ31 alloy specimens in air.

In the plastic region, the bare specimen shows the highest UTS (263 MPa) and strain (21%) values. Additionally, it is also found that the coated specimens exhibit lower UTS and strain values as compared to

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the bare one. The mechanical properties of plastic region (UTS and strain) for Al-coating, Si-coating, and P-coating samples are tabulated in **Table 8**.

Table 8. Tensile properties of the bare and PEO coated samples at room temperature.

Sample	Ultimate tensile strength (UTS) MPa	Elongation %
Bare	263	21
Al-coating	231	18
Si-coating	209	12.6
P-coating	169	7

The largest decline was observed in the P-coating, where UTS and strain were reduced by 35% and 66%, respectively. Interestingly, the reduction in YS, UTS, and strain values are inversely related to the average pore diameter and porosity percentage in the coatings. Accordingly, this drop could be attributed to the presence of the brittle ceramic coating of the PEO specimens [43]. The higher-magnification scanning electron micrograph (**Figs. 2** and **3**) revealed the presence of cracks and pores in the PEO coating as well as damaged regions exposing the substrate (**Table 4**). During early stage of PEO coating process, the establishment of cracks in the inelastic PEO-coated surface and their subsequent development into the substance can be considered to consequence of thermal stress as a result of rapid solidification of molten oxides in the arc region. Conversely, a rising stress concentration can be observable locally and preferentially on the coated samples which include numerous pores and cracks beforehand during tensile test. The latter results in far lower tensile strength and elongation compared to the uncoated one. Indeed, cracks and pores act as stress concentration regions during deformation, so YS, UTS, and strain diminish with expansion of these areas from the Al-coating to the P-coating. Furthermore, in this elastic stage, the applied deformation was reversible upon the elimination of external stress. However, the coated samples might suffer permanent damage even in this low strain stage [44]. While the specimen is tensioned by an exterior load during the tensile test, a shear stress will progress at the interface of coating and substrate; thus, there is an induced tensile stress within the coating. At adequate loads, when the induced tensile stress outstrips the tensile strength of the coating, it begins to crack. Such separation of the cracks might be caused by periodic sequential cracking of brittle coatings on elastic substrates, as suggested by [18, 45] based on a sinusoidal shear stress distribution model. A similar coating behavior has also been observed through an experiment and reported by Asquith et al. [44] as well as Hiromoto et al. [46].

4. Conclusion

The effect of an electrolytic solution was characterized on the corrosion behavior and mechanical properties of a coated AZ31 magnesium alloy via plasma electrolytic oxidation in this study. Based on the experimental results and analyses, several conclusions can be drawn as follows:

- The spark and stability voltage of PEO process and as a result, spark characteristics change under the type of electrolyte. With increasing spark and stability voltages, the thickness of the coating and the porosity increased from Al-coating to P-coating due to the intensification of the energy of spark pulses.
- The dominant phase in P-coating and Al-coating was MgO, i.e. Mg_2SiO_4 for Si-coating.
- Investigation of the correlation between the corrosion rate of coatings and the morphological characteristics of the coatings and the electrical characteristics of the process showed that in addition to the surface quality of the coating, other parameters affect the corrosion resistance of the Si-coating.
- The results of equilibrium of impedance spectra with suitable equivalent circuits revealed that in Si-coating, the major portion of the corrosion resistance of the coating was related to the inner layer. The heterogeneity of the interface of the inner and outer layers of the Si-coating caused a high amount of corrosive electrolyte contact with the coating. As a result, the high corrosion resistance of the inner layer of the coating is due to its compact, homogeneous structure and stable phase

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(Mg$_2$SiO$_4$) of inner layer. The tensile strength and elongation diminished from the uncoated to coated samples.

- Both the tensile strength and elongation dropped by changing the electrolyte from Al-coating to P-coating, while the yield strength was almost similar. The latter could be attributed to the presence of cracks and pores in the brittle ceramic PEO coating as stress concentration regions during deformation, resulting from thermal stress during the coating process and deformation in the elastic stage.

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