Production of high quality coatings on light alloys using Plasma Electrolytic Oxidation (PEO)

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Abstract

Plasma Electrolytic Oxidation (PEO) is a high voltage plasma-assisted oxidation process which involves the creation of plasma discharges around a metal surface component immersed in an environmentally-friendly aqueous electrolyte to form ceramic oxide coatings which can, if correctly formed, impart a high corrosion and wear resistance. During PEO coating, there are three simultaneous processes taking place, namely the electrochemical reactions, the plasma chemical reactions and thermal oxygen diffusion. All PEO-coatings have a three-layer structure with a porous outer layer, and intermediate dense layer and a thin inner dense layer. It is through control of the relative amounts (thickness) and composition of these three that high quality coatings can be obtained. In this paper we describe how processing parameters including current density, current mode (unipolar, bipolar, hybrid), and electrolyte (concentration and composition) effect the quality of the coatings as measured by the corrosion and wear resistance. In general terms, an intermediate current density and a bipolar current mode lead to the most compact and high quality coatings, although the growth rate is reduced compared to using a unipolar current mode and higher current densities. The growth rate can be increased by increasing the electrolyte concentration. Incorporation of silicates and aluminates into the electrolyte can result in the formation of hard spinels in the coatings, which can then lead to better wear and corrosion resistance.
Keywords: PEO coatings, coating mechanism, process parameters, corrosion, wear.

1 Introduction

Current coating schemes are complex, multilayer systems that incorporate many different technologies and must be conducted very carefully in order to adequately protect lightweight metals and their alloys from wear and corrosion in harsh service conditions. In order to achieve higher levels of protection, one of the most promising coating methods is the PEO technique. Plasma Electrolytic Oxidation (PEO) is a high voltage plasma-assisted oxidation process, considered as one of the most cost-effective and environmentally friendly ways to form a thick, ultra-hard and adherent ceramic oxide by plasma discharge of lightweight metals (Mg, Al and Ti) and their alloys [1, 2]. The PEO process involves the creation of plasma discharges around a metal component immersed in an alkaline electrolyte when a high potential is applied to it. During the PEO process, different types of discharges will take place [3, 4]. An important consequence of the occurrence of those discharges is the development of metallurgical processes in the growing oxide layer, which are induced by the heat liberated in discharge channels from electron avalanches. Because of the local high temperature and the strong electric field, molten oxide is ejected from the coating/substrate interface into the coating surface where it is rapidly solidified and re-crystallized by the electrolyte. Hence, the formation mechanisms for the coatings are complex due to the involvement of the electrochemical reactions, the plasma chemical reactions and thermal oxygen diffusion.

In general, PEO coatings on lightweight alloys have been found to have a three-layered structure as shown in Figure 1. Figure 1(a) is a SEM micrograph of a cross-section of a coated Al alloy. Figure 1(b) is a schematic diagram showing a porous outer layer, an intermediate layer that is relatively dense, and a thin inner dense (barrier) layer that is well adhered to the substrate. Although it is the intermediate dense layer that can provide good mechanical properties (eg wear) and corrosion protection, it is the inner dense layer that ultimately provides the best corrosion performance [5–9].
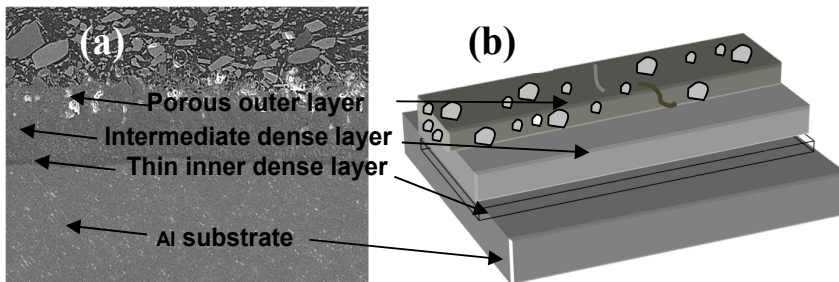

Figure 1:   PEO coating on Al alloy showing (a) SEM micrograph of cross-section. (b) Schematic diagram of layer structure [5, 9].

Many processing parameters can affect the PEO process, including electrolyte concentration and composition [10], substrate material [11], and electrical

parameters, mainly current mode and current density [8, 12]. Different current modes have been utilized in the PEO treatment including, DC, AC, unipolar, bipolar and hybrid (combination of bipolar and unipolar) current modes [13] which play important roles in the consequent voltage breakdown and discharge events, both in terms of discharge intensity and density, local melting and oxidation of the substrate, quenching and re-crystallization processes. The discharges have a profound effect on the coating microstructure, thickness, roughness, porosity, hardness, and coating growth rate, and hence affect the corrosion and wear resistance of the coated lightweight alloy.

PEO has been used to rapidly and economically produce oxide coatings on lightweight alloy components of almost any shape and size. There are various problems to be solved but there is a much bigger potential for PEO in automotive and other applications than currently used [6, 9]. Although a general picture of the PEO coating growth mechanisms [14, 15], discharge behaviour [3, 15] and resulting coating formation has been developed, a number of gaps in knowledge remain concerning processing-structure-properties-performance relationships. Further work was required in order to specify the critical parameters that would lead to more reproducible and higher performance coatings. In this paper we examine the interactive effects of PEO processing parameters, and alloy composition and microstructure, on the microstructure of the coatings and, therefore, on the resulting corrosion and tribological properties. To accomplish this, we mainly use examples from our own work on Mg-alloys, although many of the principles are equally applicable to the other light alloys based on aluminum [9, 16, 17] or titanium [8, 18].

2   PEO-coating mechanisms

The growth of the PEO oxide coating mainly occurs due to three different, yet simultaneous, processes, namely: the electrochemical reactions [1], the plasma chemical reactions [19] and thermal diffusion [20]. Fig. 2 is a schematic of the PEO coating growth process on a magnesium alloy substrate. The main electrochemical reactions occur at the coating/electrolyte interface, through different mechanisms depending on the electrolyte. According to the study by Yerokhin *et al*. [21], oxide layer formation is induced both by the ionic component of the current, which is transmitted via surface discharges, and by the anodizing current passing across the surface, which is free of discharges.

The plasma chemistry of the surface discharges involves, on one hand, charge transfer at the substrate/electrolyte interface, and on the other hand, strong ionization and charge transfer effects between the substrate surface and the electrolyte through the oxide layer with the aid of the plasma. During the PEO process different types of discharges will take place [5]. An important consequence of the occurrence of those discharges is the development of metallurgical processes in the growing oxide layer, which are induced by the heat liberated in discharge channels from electron avalanches. The ceramic coating grows inwards to the alloy substrate (inner layer) and outwards to the coating surface (outer layer) simultaneously [15].
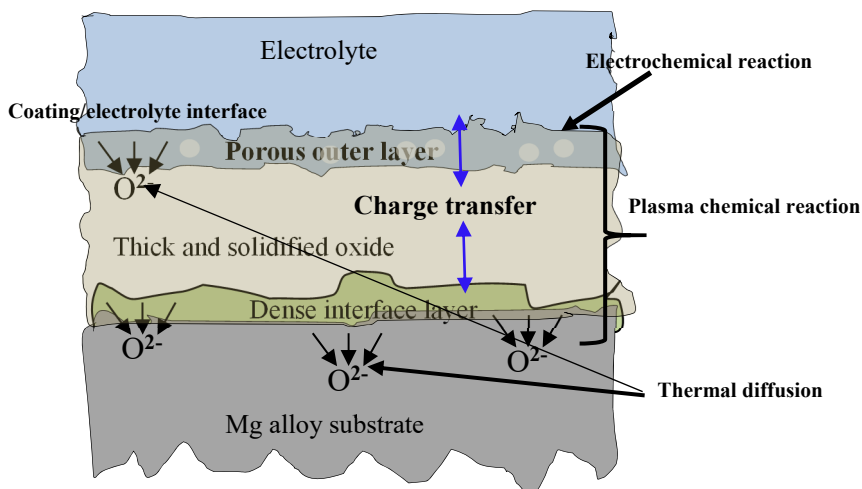
Figure 2:   Schematic of a PEO coating growth process on a Mg-alloy substrate.

Both thermally-activated diffusion and anion transfer have an important contribution to coating growth [22]. Inward oxygen diffusion into the alloy substrate plays a key role in coating growth. The growth rate is influenced by the plasma temperature, which enhances the rate of oxygen transport towards the magnesium substrate as shown in Fig. 2. Hence, the rates of growth of the outer and inner oxide layers results from a combination of three processes namely, (i) discharge processes causing the substrate to melt and oxidize when flowing out through the discharge channels and being rapidly cooled at the surface–electrolyte interface, (ii) partial destruction of the outer layer due to strong discharges and (iii) diffusion of oxygen process from the electrolyte towards the substrate through the coating.

3   Plasma discharge effects on microstructure of coating and properties

Quantitative studies have been performed by our group relating processing to performance [6, 13, 15, 16, 22, 23]. It has been confirmed that a PEO processing of Mg alloys is strongly influenced by such parameters as electrolyte chemistry, current mode and density and substrate alloy. The effects of these PEO process parameters on the coating quality and properties are discussed in more detail in sections 3.1 to 3.3.

3.1 Current mode and current density effects

With the aim of improving the characteristics of the PEO coatings, many attempts [4, 5, 20] have been made to improve the supplied current regimes, suggesting different forms and duration of the current pulses. Four different current modes (unipolar, bipolar and hybrid (unipolar-bipolar and bipolar-unipolar)) were used in the PEO processing of Mg-alloy AM60B in a mixed aluminate and phosphate electrolyte [22, 24]. Changing the current mode produces changes in the PEO

process characteristics, including the breakdown voltage and discharge events, both in terms of discharge intensity and density [22]. Increasing the current density and/or voltage led to an increase in layer thickness, as well as enlargement of the surface craters.

Fig. 3 shows the SEM micrographs of the coating surfaces and coating cross-sections on AM60B [22]: H11 treated using unipolar current mode only for 15 minutes, H12 by completing the treatment of H11 using bipolar current mode for another 15 minutes; H21 treated firstly using bipolar current mode; H22 completed the treatment using unipolar mode for second 15 minutes. Controlling or reducing the strong discharges (by bipolar current mode, appropriately controlling the ratio of the positive to negative pulse currents as well as their timing) had a significant positive effect on the plasma temperature profiles and leads to denser inner layer microstructures with less porosity. The order of the combined current modes is essential. Hybrid1 case improves the coating quality compared to other cases as the bipolar mode acts to repair the damage caused by the unipolar mode.

The role played by current density using bipolar current modes on the microstructural characteristics of oxide coatings produced on a AZ91D Mg alloy in an electrolyte of 8 g/l Na2Al2O4and 1 g/l KOH was also investigated using the process parameters given in Table 1 [23]. Although increasing the cathodic current density from 0.05 A/cm^2 to 0.11A/cm^2 produced a thicker coating (thickness increased from 22µm to 60 µm), there was a corresponding increase in coating defects, including porosity and microcracks.

Corrosion testing of the coated samples was conducted using EIS and results are shown in Fig. 4.

All PEO coatings offered significant corrosion protection to the AZ91D alloy. The Bode impedance diagram (Fig. 4(b)) shows the impedance modulus in the LF range, varies from $10^{5.5}$ Ω cm^2 to $10^{6.5}$ Ω cm^2 for S1and S2 but is much lower ($10^{3.1}$ Ω cm^2) for S3 which is coated at a high current density [23]. Compared to uncoated alloy, the high impedance and high polarization resistance values in the EIS results demonstrated that the PEO coating did not undergo any significant degradation and that the coating at the metal-substrate interface was providing significant protection. It is concluded that the corrosion protection performance of the PEO coatings is indirectly dependent on the current density and is controlled by the amount of porosity and other coating defects which could control the penetration rate of the electrolyte through the PEO coating [23].

Similar effects of current mode have been found for aluminium alloys. Fig. 5 shows the cross sections of an AA5052 Al alloy coated using either unipolar (Al 1) or bipolar current modes (Al 2 coated for 60 min and Al 3 coated for 90 min respectively) [17]. Al 1, coated using the unipolar current mode, shows a significant amount of connected porosity, holes and other structure defects within the coating and near the coating/substrate interface, Fig 5(a). The cross-sections of samples Al 2 and Al 3 shown in Figs 5(b) and (c) which were obtained using pulsed bipolar current mode with different treatment times, show that the surface/coating interface was smooth and almost free from porosity and defects. Compared to the sample Al 2, the sample Al 3 showed a thicker coating with relatively less porosity in the inner layer.
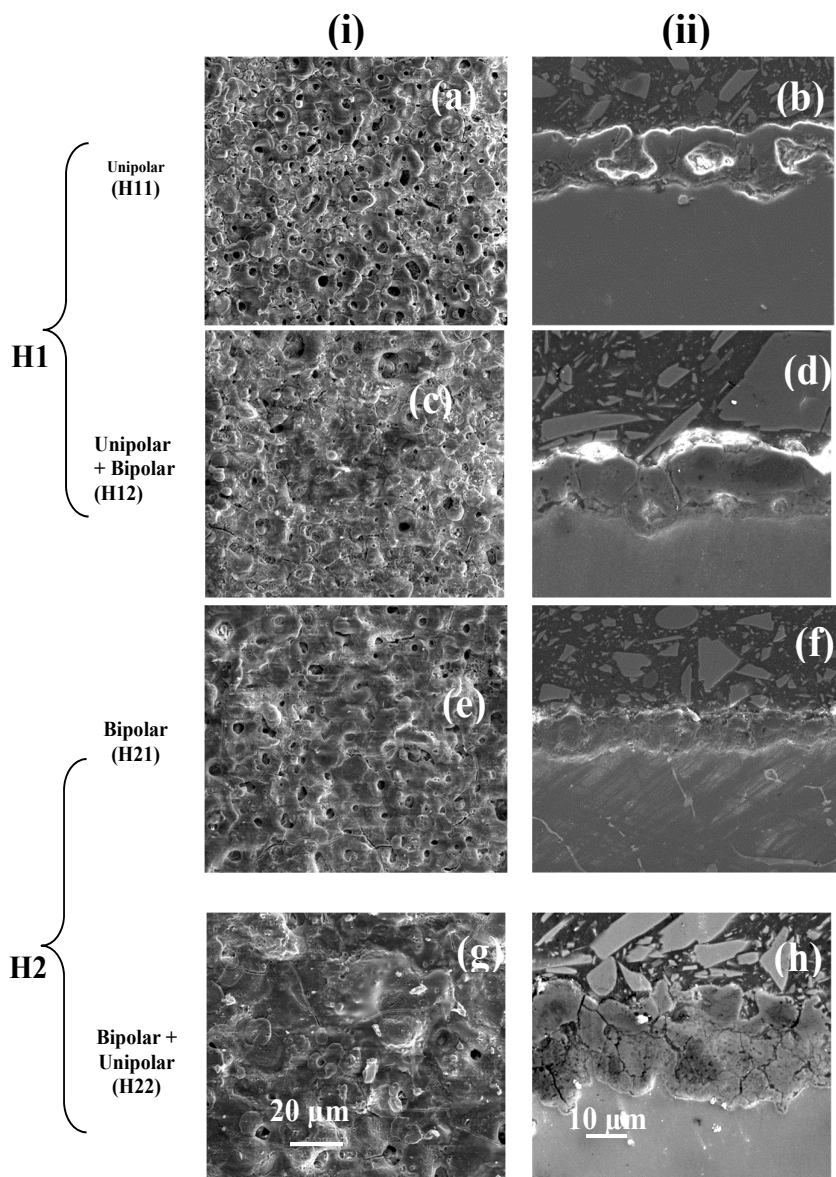
Figure 3: (i) Morphology of oxide coatings on Mg AM60B magnesium alloy using secondary electron mode (SE) (ii) SEM micrographs of polished sections of coatings using secondary electron mode (SE) and for: (a), (b) unipolar H11, (c, d) hybrid1 (uni + bipolar), (e), (f) bipolar H21 and (g), (h) hybrid2 (bi + unipolar) current modes [22].

Table 1:   PEO process parameters for coating AZ91D Mg alloy [23].

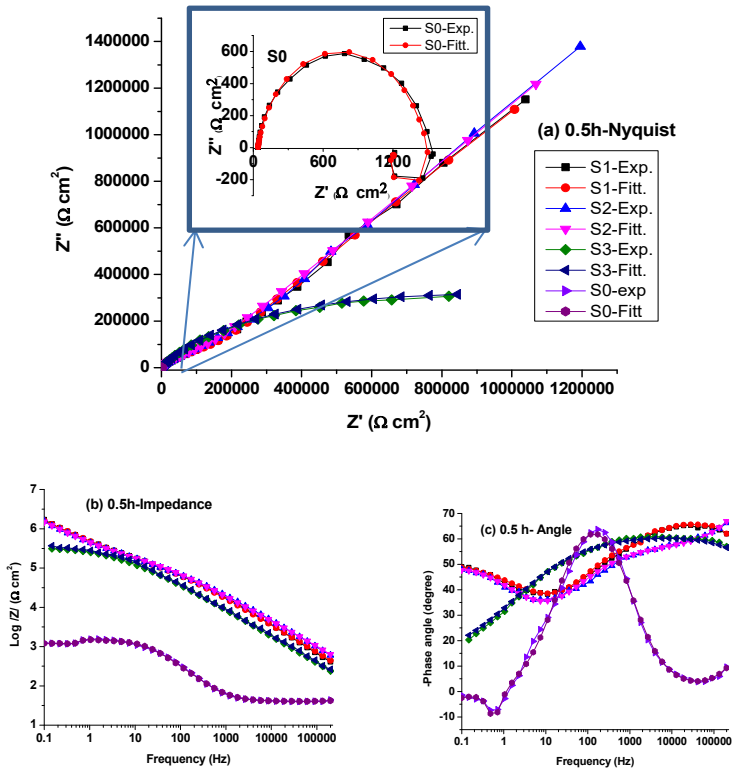| S	Current mode	Time (min)	I^+ (A)	J^+ (A/cm^2)	I^- (A)
S1	Bipolar	30	0.68	0.05	0.5
S2	Bipolar	30	0.95	0.07	0.7
S3	Bipolar	30	1.5	0.11	1.1

Figure 4:   EIS plots of coated (S1-S3) and uncoated (S0) AZ91D Mg alloy at different current densities for 0.5 h immersion time ((a) Nyquist, (b) Impedance and (c) angles plots) [23].

The potentiodynamic polarization curves of the uncoated AA5052 Al alloy (Al 0) and the PEO coated specimens using either unipolar (Al 1) or bipolar current modes (Al 2 and Al 3), Fig. 6, clearly show the enhanced corrosion resistance afforded by the coatings. In contrast to the uncoated AA 5052, all PEO coated samples had more positive corrosion potentials and lower corrosion current densities. By using bipolar current mode the corrosion resistance increased from 31 MΩ /cm^2 for the uncoated alloy to 2631 MΩ /cm^2 [9].
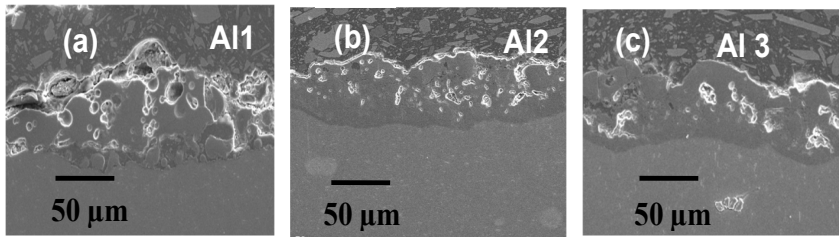
Figure 5:   SEM micrographs of cross-section morphology of oxide coatings on Al AA5052 alloy for: (a) unipolar Al1, (b), (c) bipolar Al2 and Al3 coated for 60 min and 90 min respectively [17].
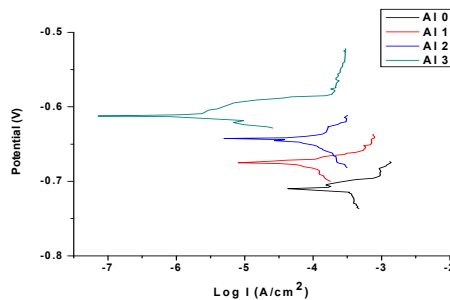

Figure 6:   Potentiodynamic polarization curves in 3.5% NaCl solution of the uncoated (Al0) and coated 5052 Al alloy samples using unipolar (Al1) and bipolar (Al2-Al3) current modes [9].

The last example will explain the role played by current modes on the microstructural and tribological characteristics of oxide coatings produced on a AM60B Mg alloy in a 7g/l $K_4P_2O_7$ + 3 g/l $Na_2Al_2O_4$ and 1 g/l KOH electrolyte [24]. A unipolar current mode gives rise to thicker (≈48 μm), more porous (amount and size) coatings with a higher surface roughness than those produced using a bipolar current mode (≈37 μm) or H1(U+B) and H2 (B+U) modes (≈30 μm) [24]. As shown in Fig. 7, the denser coatings with lower surface roughness that are produced by the B and H1 current modes compared to the U and H2 modes lead to improved tribological performance in both pin-on-disk (Fig. 7(b), and inclined impact–sliding tests.

3.2 Alloy composition effects

The effect of substrate composition on the PEO coatings microstructure and properties for pure magnesium and magnesium alloys AM60B (Mg – 6Al – 0.2Zn), AJ62 (Mg – 6Al – 2Sr) and AZ91D(Mg – 9Al – 1Zn) was investigated [25]. The variation of the average total coating thickness with PEO treatment time is shown in Fig. 8. The coating thickness increases linearly with coating time which is in good agreement with most other PEO experiments [26]. For the bipolar current mode, the average growth rate was 0.9 ± 0.05 μm/min. However, AZ91D
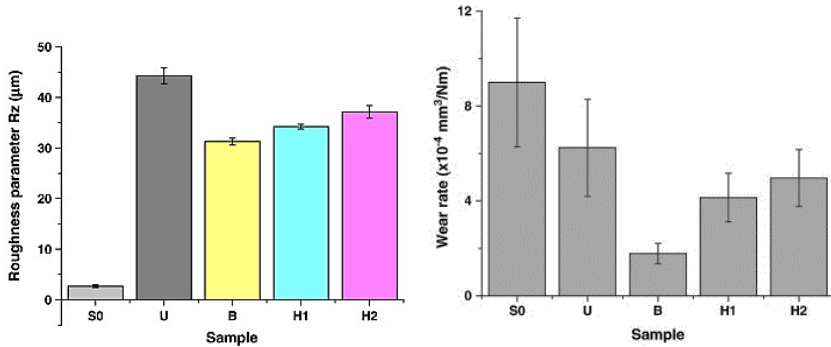
Figure 7:   (a) Roughness parameter Rz and (b) Wear rates of the oxide coatings formed using different current modes and the uncoated Mg alloy substrate [24].

Mg alloy shows a relatively higher coating thickness compared with other samples.

Each coating has a different phase composition and surface morphology due to the effect of the different alloying elements. Electrochemical impedance spectroscopy (EIS) corrosion testing showed that the bipolar PEO coated AZ91D Mg alloy had a higher corrosion resistance when compared to coated AM60B, AJ62 and pure Mg. The ranking for corrosion resistance in 3.5% NaCl was Mg uncoated < coated pure Mg < coated AJ62 < coated AM60B < coated AZ91D which is consistent with the average coating thickness results.
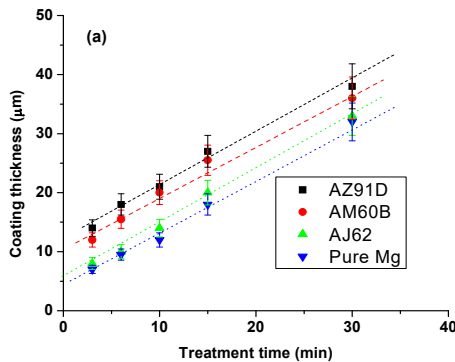

Figure 8:   Average coating thickness variation with PEO processing time for different Mg alloys [25].

3.3 Electrolyte concentration and composition effects

PEO coatings on Mg alloys and other lightweight alloys are normally produced using environmentally friendly base electrolytes (NaOH/KOH) with the addition of silicate, aluminate, phosphate or polyphosphate-containing alkaline electrolytes to increase the conductivity of the electrolyte solution. To illustrate the effects of electrolyte composition and concentration on the coating quality, we will use our

Table 2:   Electrolyte composition for PEO processing of AZ91D.

Sample	KOH (g/l)	Na₂Al₂O₄ (g/l)	Na₂WO₄.2H₂O (g/l)
S1	2	8	0.0
S2	2	8	1.0
S3	2	8	2.0
S4	2	8	6.0
S5	2	15	0.0

work on an AZ91D magnesium alloy which was PEO-coated using a base KOH electrolyte with additions of aluminate ($Na_2Al_2O_4$) and tungstate (Na_2WO_4) as detailed in Table 2 [27].

Table 3 provides a summary of the breakdown voltage at which sparking occurs, coating thickness, colour and composition (at surface). With increasing electrolyte concentration, the breakdown voltage is decreased and a thicker coating is produced. Increasing aluminate concentration led to a higher aluminium content in the coating and a higher tungstate addition led to a higher tungsten concentration in the coating.

Table 3:   Breakdown voltage and time, thickness, color and composition of coating.

S	Breakdown		Coating thickness. (μm)	Color	Composition (wt%*)			
	v(V)	t(min)			O	Mg	Al	W
S1	390	2.0	25±2.5	Gray	37.3	33.3	29.1	0.0
S5	360	1.5	23±2.3	Gray	38.3	26.9	34.7	0.0
S2	375	0.50	30.0±3	Gray/light green	37.4	33.4	26.8	2.3
S3	360	0.40	29±2.9	Gray/medium green	36.1	30.7	30.1	3.1
S4	280	0.25	43±4.5	Green with black spots	35.2	29.4	26.9	8.6

*As measured at the surface of the coatings using EDS.

XRD spectra of all PEO-coated samples are shown in Fig. 9(a). Detailed identification of the phases present for samples S1 and S4 are given in Fig. 9(b) and (c), respectively.

For S2, S3, S4 samples as well as MgO, and an increased amount of $MgAl_2O_4$, the tungsten containing phases WO_3 and $MgWO_4$ are also present. The addition of 6g/l tungstate (S4), Fig. 9(c), causes the amorphous phases to disappear leaving the hard spinel $MgAl_2O_4$ phase, and creates the new phases, WO_3 and $MgWO_4$ which cause the greenish color with some black spots on the samples. The existence of $Na_2WO_4.2H_2O$ in the electrolyte will cause some of the WO_4^{2-} ions to lose the electrons forming the black WO_3 compound. The main electrochemical reactions occurring during the PEO process in tungstate-containing electrolytes are as follows [27]:

$$2WO_4{}^{2-}- 4e^-\rightarrow 2WO_3+O_2 \uparrow \qquad (1)$$

$$WO_3+ 3Mg \rightarrow 3MgO+W \qquad (2)$$

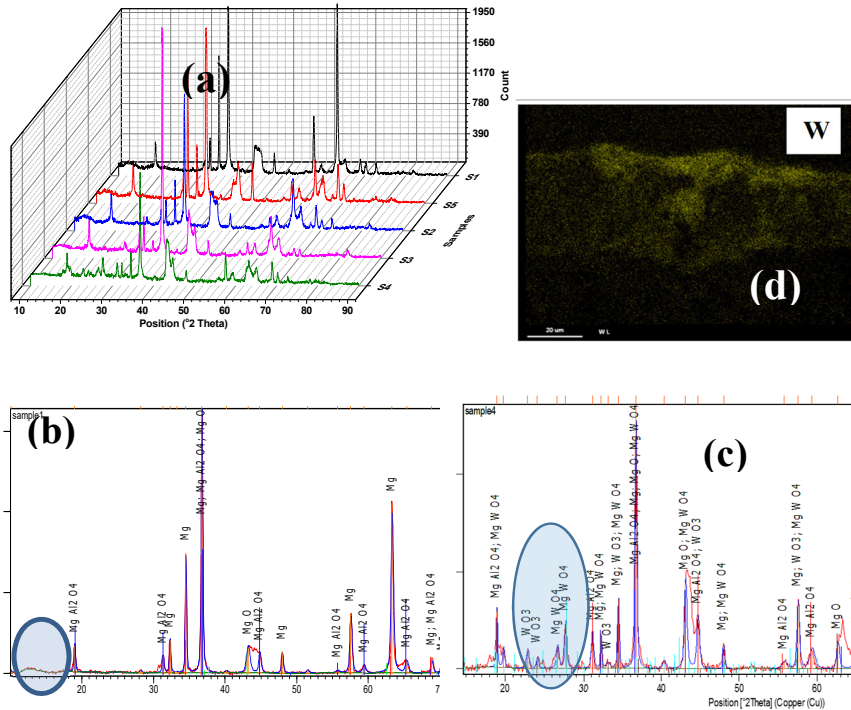Fig 9(d) shows that the tungsten was deposited all through the coating cross section.

Figure 9:   XRD patterns of oxide coatings formed in aluminate-KOH electrolyte with addition of different concentrations of Na$_2$W0$_4$: (a) all samples (b) 0 g/l Na$_2$W0$_4$, (c) 6.0 g/l Na$_2$W0$_4$ and (d) EDX tungsten (W) mapping of cross-sections of AZ91D Mg alloy PEO coated sample S4 [27].

Potentiodynamic polarization corrosion testing of all samples was conducted in 3.5% NaCl and the results are shown in Figs 10(a), (b). Compared to the uncoated AZ91D, all PEO-coated samples exhibited a higher polarization resistance, a lower corrosion current density and a higher (more noble) corrosion potential than the uncoated alloy (S0). The electrolyte concentration and composition directly influences the surface morphology, coating microstructure, porosity level, thickness and phase composition of the coatings, which, in turn, affects the corrosion performance. Increasing the aluminate concentration in the electrolyte from 8 to 15 g/l, produces a coating that is denser and contains a higher amount of the spinel phase relative to MgO. This produces a more corrosion resistant coating: see Fig. 10(a). The addition of tungstate to an electrolyte containing 8g/l aluminate increases the conductivity of the electrolyte, lowers the break-down potential, lowers the porosity/defect density of the coatings, increases the coating growth rate and produces a thicker substrate/coating interface layer, increases the MgAl$_2$O$_4$ spinel phase content, and leads to the formation of the tungstate-containing phases WO$_3$ and MgWO$_4$. All these factors lead to an improvement in corrosion resistance: see Fig. 10(b).
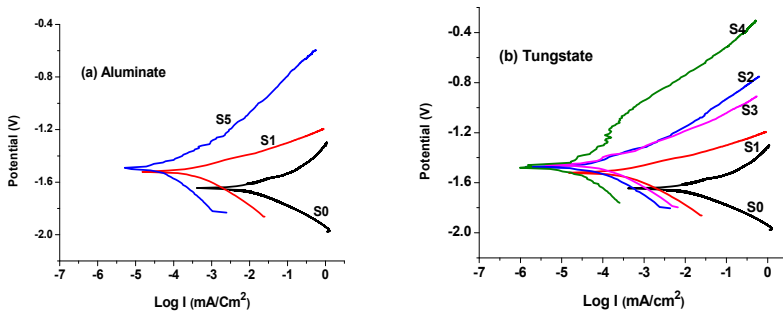
Figure 10: Potentiodynamic polarization curves of the uncoated (S0) and coated samples with (a) different aluminate concentrations (S1 and S5) and (b) different tungstate concentrations (S1–S4), for 0.33h immersion time [27].

4 Relationships between processing parameters and performance

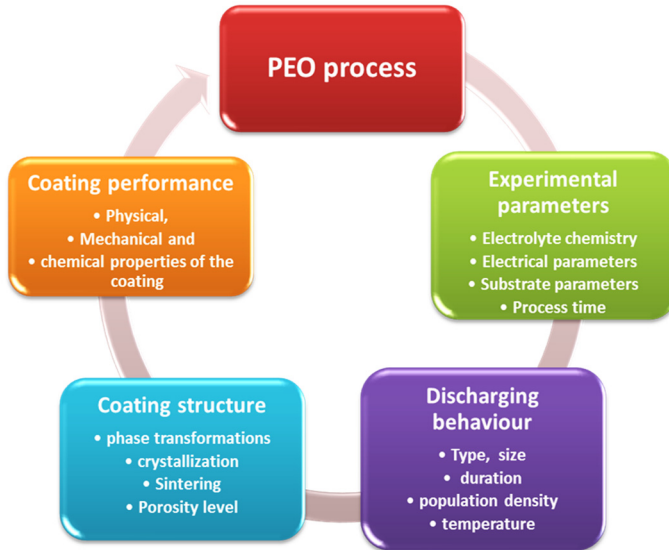A schematic describing these general relationships is given in Fig. 11.

Figure 11: Relationships between PEO processing parameters, discharge behaviour, coating structure and performance.

The main conclusions are:
- The PEO processing of light alloys is strongly influenced by such parameters as electrolyte composition and concentration, current or voltage applied and substrate alloy.
- Generally, these parameters have a direct influence on the discharging behavior: type, size, duration, population density and temperature.
- The discharges play an essential role in the formation, relative thickness and resulting composition of the 3-layer oxide structure, by influencing phase transformations, crystallization and sintering.
- This, then, affects the physical, mechanical and chemical properties of the coating.
- The corrosion performance is more closely related to the protective nature of the dense oxide layer at the coating–substrate interface.
- The wear performance is effected mainly by intermediate layer. Since the coating is integral with the substrate, there is good adhesion.

5   Recommendations for production of high quality coatings

Tables 4–6 summarise the process parameters effects on the coating quality and makes recommendations for the production of high quality coatings.

Table 4:   The effect of current density and current mode on the coatings.

Process parameter	"Value"	Effect on Coating
Current Density	low	Low growth rate; more compact
	high	High growth rate; less compact
Current Mode	Unipolar (U)	Higher growth rate; less compact
	Bipolar (B)	Low growth rate; more compact
	Hybrid (B+U)	Intermediate growth rate; less compact
	Hybrid (U+B)	Intermediate growth rate; more compact

Recommendation: Intermediate current density + Bipolar Mode = best coatings.

Table 5:   The effect of the substrate composition on the coatings.

Substrate	Composition	Elements from substrate can incorporated into coating. Generally for Mg-alloys, the growth rate of the coating after initial processing period is independent of alloy composition.

Recommendation: PEO coating is applicable to all lightweight alloys regardless of their composition. However, the growth rate and phase composition/porosity of coatings is composition dependent.

Table 6: The effect of the electrolyte chemistry on the coatings.

Electrolyte	Concentration	Higher concentration increases conductivity, decreases breakdown voltage, thereby increasing growth rate.
	Composition	Addition of aluminate and silicate can induce formation of spinels in coating. Higher hardness, better wear properties, and improved corrosion resistance. Tungstate addition can provide inhibitive effect and improved corrosion resistance.

Recommendation: tailor the electrolyte to produce coating with desired phases/properties.

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