Plasma electrolytic oxidation (PEO) coatings on Mg-alloys for improved wear and corrosion resistance

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Abstract

Due to their high chemical reactivity, relatively low melting point and low hardness, magnesium and magnesium alloys have relatively poor corrosion and wear resistance. Since both corrosion and wear are surface phenomena, a number of surface engineering techniques have been used to improve corrosion and wear performance. Whilst some surface hardening/strengthening methods have led to improvements in wear properties, they have not, in themselves, significantly improved the corrosion performance. Plasma electrolytic oxidation (PEO) has the potential to produce hard, compact oxide coatings that are well adhered to the magnesium alloy substrate. Such coatings can provide both improved wear and corrosion resistance. In this paper we describe how by changing the PEO processing parameters (substrate alloy; electrolyte; current or voltage; processing time) we can change the nature of the PEO oxide coatings (thickness; microstructure; porosity; phase content; composition) which, in turn, effects the corrosion and wear performance. All PEO-coatings have a three-layer structure with a porous outer layer, and intermediate dense layer and a thin inner dense layer. From a corrosion aspect, the performance of coatings is determined by the time taken for corrosion to initiate since this is much shorter than time taken for the coating to degrade. For PEO-coated Mg-alloys, this initiation time is primarily determined by the thickness, porosity and phase content of the inner dense layer at the coating/substrate interface. With respect to tribological properties, the coefficient of friction (COF) in dry sliding wear increases with increasing surface roughness of the PEO coatings. The wear rate is primarily determined by the thickness and hardness of the intermediate dense layer.

Coatings containing less porosity and higher spinel-phase ($MgAl_2O_4$, Mg_2SiO_4) content are harder and more wear-resistant.

Keywords: magnesium alloys, PEO coatings, three-layer structure, corrosion, tribological properties.

1   Introduction

Magnesium is the lightest structural metal. In addition to its low density, a high specific strength, specific stiffness, good castability and weldability, good damping, and good electro-magnetic shielding make magnesium alloys a desirable material for many applications [1]. However, their lower formability, relatively low creep resistance at elevated temperature and high chemical reactivity with associated low corrosion and wear resistance, limits the use of magnesium alloys in many industries [2].

It is generally recognized that magnesium has poor wear resistance and that this is related to a low hardness [3]. The main mechanism for improving the mechanical properties is precipitation hardening, e.g. by adding aluminum which forms an $Mg_{17}Al_{12}$ intermetallic phase which increases tensile strength and hardness. However almost all elements used so far for alloying increase magnesium's susceptibility to corrosion. The relatively poor wear performance of magnesium and its alloys is also related to magnesium's high reactivity and relatively low melting point. Surface treatment to form coatings which produce a protective ceramic, polymer or composite layers is considered as one of the most effective ways for corrosion and wear protection. Such coatings should be uniform, pore free, relatively thick, hard, well adhered, flexible to withstand an overload, and insulating to minimize corrosion. Plasma electrolytic oxidation (PEO) fulfills most of these requirements and has been used for depositing a well adhered ceramic coating on light-weight metals (Mg, Al, Ti) that provides not only corrosion protection but also enhanced wear properties, hardness and toughness with better thermal stability and dielectric properties [4, 5].

Plasma Electrolytic Oxidation (PEO) is a process that transforms the magnesium metal surface into thick, ultra-hard ceramic oxides by a plasma discharge in an electrolytic bath [6, 7]. The PEO process for light-weight metals is strongly influenced by such parameters as electrolyte composition and concentration, current or voltage applied, and substrate alloy [8]. Generally, these parameters have a direct influence on the phase transformations, crystallization and sintering.

Due to the existence of temperature gradients between the inner and outer layer of the coating, PEO coatings on light alloys have been found to have a three-layered structure [6]. The porous outer layer usually has poor mechanical properties. The intermediate layer is relatively dense and can provide good corrosion protection. The third (barrier) layer is a very thin interface layer (few hundred nm to 1 μm in thickness) is well adhered to the substrate and ultimately provides the best corrosion performance [6]. Mg alloy parts used for automotive and aerospace applications including helicopter gearbox covers, pistons and cylinders, are subject not only to corrosion but also to mechanical wear.

Relatively few published papers can be found that combine both tribological and corrosion studies of PEO treated Mg alloys. In this paper we use primarily our own work to illustrate the general relationships between PEO processing parameters and the subsequent tribological-corrosion performance of the coatings.

2 Corrosion and tribological properties of PEO coated Mg-alloys

2.1 Corrosion resistance

Magnesium alloys exhibit very poor corrosion resistance due to their chemically active nature, especially internal galvanic corrosion [9], which can further cause severe pitting corrosion on the metal surface resulting in decreased mechanical stability and an unattractive appearance. For coated metals, including Mg-alloys, the corrosion performance of coatings is determined by the time taken to initiate corrosion in the metal substrate since this is much shorter than the time taken for the coating to degrade [10]. Generally the corrosion resistance of PEO-coated magnesium alloys depends on many factors that are summarized schematically in Fig. 1. The overall protective abilities of the PEO coatings are governed by:
  – Coating structures, mainly coating compactness in terms of porosity and other defect levels
  – Relative thicknesses of the three layers, particularly the coating/substrate interface layer,
  – Chemical composition of the coating.
Therefore, the more compact and thicker the coating layers, the more difficult it is for the corrosive anions or oxidants (Cl^{-1} ions) to penetrate to the base magnesium substrate. The coating/substrate barrier layer plays a key role in decreasing the substrate area exposed to the aggressive solution. The phases present in the oxide coatings are also important in the overall corrosion resistance. The spinel phases ($MgAl_2O_4$, Mg_2SiO_4) are more resistant to dissolution than MgO which can quite readily be converted to $Mg(OH)_2$ [11].

2.2 Mechanical/tribological properties

As a result of the PEO coating process, the magnesium alloy surface is converted into ceramic-like coating layers that are hard, well adhered to the substrate and wear resistant [12, 13]. PEO coatings mechanical and tribological properties depend on the characteristics schematically shown in Fig. 1:
  – Hardness is strongly dependent on the coating thickness, the nature of the dominant phases present, their ratio and distribution, and the density of porosity and micro-cracks in the coatings [7, 14, 15].
  – The adhesion is influenced by the coating thickness. As the coating process progresses, significant changes take place in the inner layer structure as result of diffusion processes [12] and adhesion is improved.

    – The load that can be supported is affected by the coating thickness. Thicker coatings will give lower stresses at the coating-substrate interface and hence give better load support [7].

– The wear resistance of coatings mainly depend on hardness, coefficient of friction and roughness. Hence, porosity levels, chemical composition, thickness, and structure of the coatings are key parameters for wear performance of Mg alloys [14]. As coating growth continues, the coating surface roughness and outer layer porosity level will increase with increasing processing time.
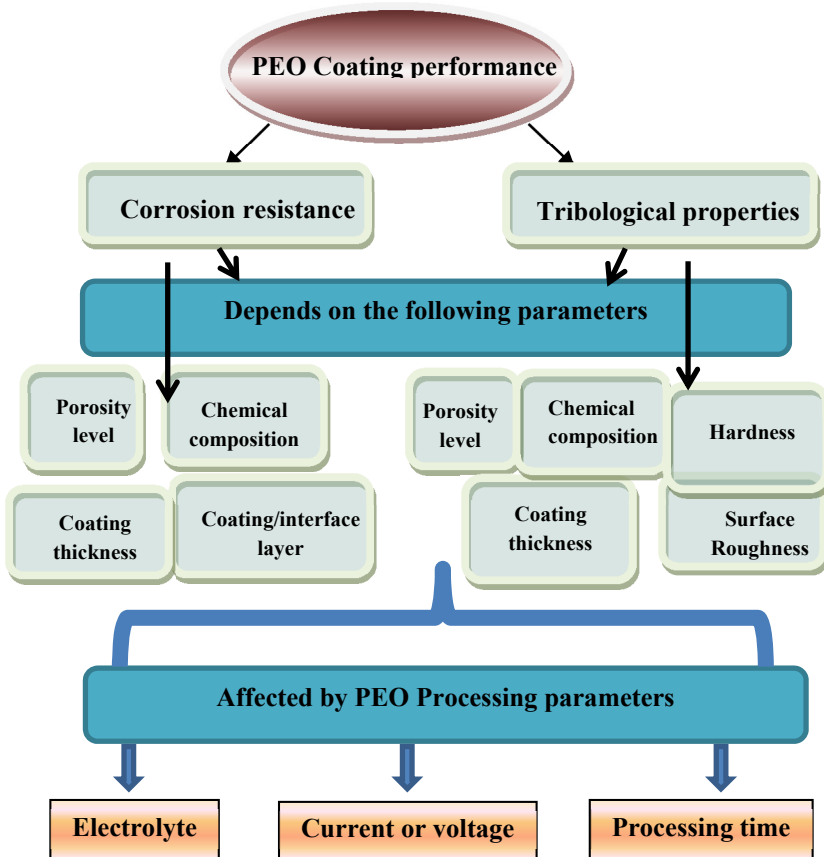

Figure 1:   PEO processing parameters and performance.

2.3 Correlation between tribological and corrosion properties

Since the coating hardness depends directly on the coating compactness, coatings produced with more porosity have lower hardness. Hence, a change of the process parameters, such as a current density and modes [5, 14] and electrolyte composition and concentration [4], are important in controlling porosity levels to improve coating hardness. Coatings produced in silicate solutions generally

have a higher hardness than coatings produced in a phosphate solution under the same process conditions [15] since the oxide layers made in a silicate solutions contain Mg_2SiO_4, which has a higher micro-hardness than MgO, $MgAlPO_5$ and $Mg_3(PO_4)_2$ that are produced in phosphate solutions[4]. The use of sodium aluminate ($NaAlO_2$) in the electrolyte for AJ62, AM60B and AZ91D Mg-alloys was investigated using different current modes [5, 6]. PEO coatings can increase the hardness of the magnesium alloys 5–9 times compared with the hardness of the base substrate [14]. However, the values of micro-hardness close to the substrate/coating interface generally have the highest value compared to other locations, which may be attributed to its higher compactness compared with the outer porous layer [16]. The wear resistance of the coated samples is a complex process that involves surface roughness and hardness which are controlled by phase contents and porosity levels.

Since PEO coatings contain unavoidable pores, although most of them are discontinuous and the number of through thickness pores is very small, the overall corrosion resistance of PEO coated magnesium alloy depends on the retarding effect of the oxide layer porosity level and on the substrate/coating interface corrosion resistance [6]. However, the more compact and thicker the coating and presence of phases more, the slower and more difficult access of the corrosive species can be. The electrochemical behaviour of magnesium alloys and PEO coatings have been mostly studied using potentiodynamic polarization in 3.5% NaCl solution at 25ºC and Electrochemical Impedance Spectroscopy (EIS). The presence of a PEO coated layer on the magnesium alloys causes a decrease of the corrosion current density by up to four orders of magnitude [6]. There are situations where the structures for good corrosion and wear performance are not the same. An example would be for oil-lubricated wear where the presence of a porous outer layer in the PEO coating could act as an oil reservoir, improving wear performance [17].

3   Illustrative examples from our own work of how to improve both the corrosion resistance and tribological properties of PEO coatings as a result of changing the process parameters

In this section we illustrate how a coating can be formed with both good corrosion and wear properties by varying the PEO process parameters, in particular the electrolyte chemistry (concentration, composition) and current mode.

3.1 Experimental procedures

Commonly used Mg-alloys AZ91D (mass fraction: Al 9%, Mn 0.15%, Zn 0.8%,Si 0.1%, balance Mg), AM60B (mass fraction: Al 5.6–6.4%, Mn 0.26–0.4%, Zn $\leq$ 0.2%, balance Mg) and AJ62 (mass fraction: Al 6.1%, Mn 0.34%, Sr 2.1%, balance Mg) are used as example materials. The PEO coating system used to produce the oxide coatings consists basically of a container with the alkaline

electrolyte and an electrical source, and is described in more detail in ref [5, 12]. A stainless steel plate in the bath acts as a counter-electrode (cathode) with the Mg-alloy coupons as the anode. The electrodes are connected to two pulsed DC power supplies operating under a constant current control function to generate different current waveforms.

3.2 Effect of electrolyte chemistry

3.2.1 Electrolyte concentration

PEO coatings were produced on AZ91D Mg-alloy using a base composition of 2 g/l KOH electrolyte and addition of two different aluminate $Na_2Al_2O_4$ concentrations 8g/l (S1) and 15g/l (S2). The PEO-coated materials show a higher coefficient of friction (COF), Fig. 2(a), but a lower wear rate, Fig. 2(b), than the uncoated alloy.

As shown in Fig. 2(c), the XRD pattern of the oxide coating made using a concentrated aluminate electrolyte, the coatings were mainly composed of MgAl2O4and MgO phases. Based on the potentiodynamic polarization and EIS results (shown in Figs. 2(d) and (e)), it was found that all PEO coatings offered significant corrosion protection to the AD91D alloy for short immersion times (0.33h hour) prior to corrosion testing.

Compared to uncoated alloy, the corrosion rate from potentiodynamic polarization was reduced by at least 50–300 times for S1 and S2, respectively. The EIS results demonstrated the same trends. As can be seen from Fig. 2(e) the impedance response of the uncoated Mg alloys (the enlarged graph) is very different from that of the coated specimens. The differences in impedance are related to the corrosion protection mechanisms for the alloys provided by the naturally formed oxide layer (few nm) which is easily corroded by the corrosive electrolyte. Sample S2, produced with a concentrated aluminate electrolyte, shows that both the tribological and corrosion properties can be enhanced at the same time. 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 $MgAl_2O_4$ relative to MgO. This produces a more corrosion and wear resistant coating. The thickness, porosity and defect levels are decreased by using a concentrated aluminate containing electrolyte.

3.2.2 Electrolyte composition

The electrolyte composition plays a key role in the PEO process and polyvalent metal anions, such as tungstate, are promising for the formation of coatings of different chemical compositions that enhance both corrosion and tribological performances. PEO coatings were produced on AZ91D Mg-alloy using a bipolar current mode and an electrolyte with a base composition of 8g/l $Na_2Al_2O_4$ + 1g/l KOH and additions of 0, 1, 2 and 6 g/l of Na_2WO_4 [18]. The Nyquist and the Bode (frequency dependencies of impedance modulus |Z|) diagrams from the EIS analysis of experimental and fitted curves of uncoated and PEO-coated materials for 0.33h immersion time are given in Fig. 3. Table 1 summarizes all the fitted EIS results for the uncoated and PEO coated samples.
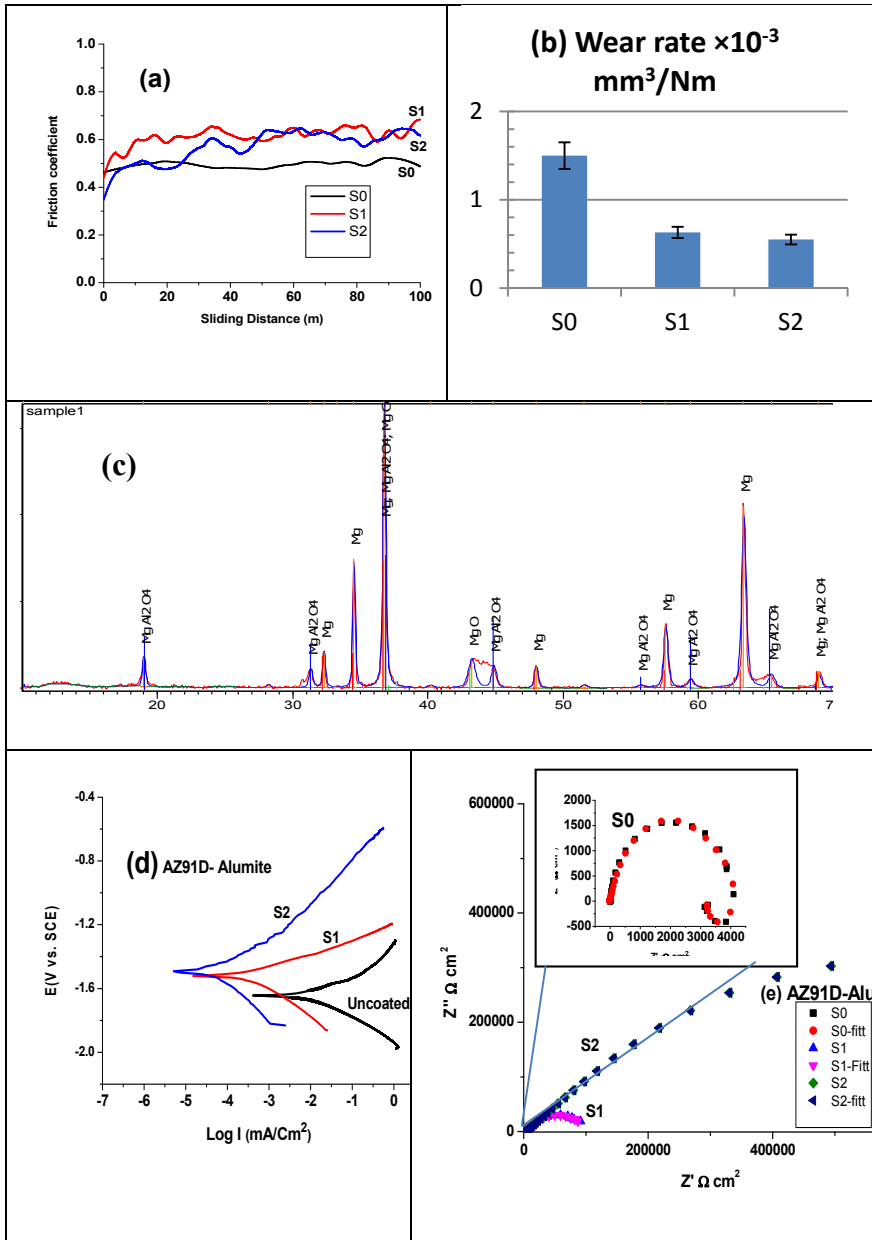
Figure 2:   (a) Coefficients of friction vs. sliding distance for samples S1 and S2 and S0 uncoated Mg alloy substrate (b) Wear rates of the oxide coatings on AZ91D alloy for different electrolyte concentrations (c), XRD pattern for S2 and (d) potentiodynamic corrosion resistance and (e) EIS results.

Table 1:　Tungstate composition, thickness and fitting results of EIS diagrams in 3.5%wt NaCl solution, for 0.33h immersion time of the uncoated (S0) (Eq. circuit Rs+CPE1/(R1+ CPE2/R2+L)) and of PEO treated AZ91D Mg alloy using four different tungstate concentration (Eq. circuit Rs+ CPE1/(R1+ CPE2/R2)).

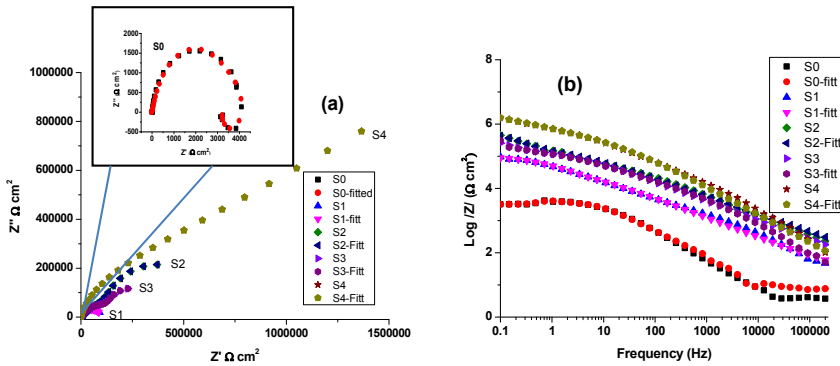| S	$Na_2WO_4 g/l$	Coating thickness μm	CPE1-Q $\mu F/cm^2 s^{1-n}$	CPE1-n	R1 $K\Omega \cdot cm^2$	CPE2-Q $\mu F/cm^2 s^{1-n}$	CPE2-n	R2 $K\Omega \cdot cm^2$	L H*
S0	----	0	18.66	0.73	-15.65	-2.498	0.33	18	0.25
S1	0.0	25.2±2.5	3.499	0.621	0.049	1.235	1	270	
S2	1.0	30.0±3.0	1.247	0.563	0.244	1.528	1	899	
S3	2.0	28.5±2.9	1.38	0.584	0.324	0.001	0	710	
S4	6.0	43.4±4.5	0.187	0.675	0.978	0.907	0.713	2269	

*Only applicable to uncoated material.

Figure 3:　Plots of uncoated and PEO coated AZ91D Mg alloy after 0.33h immersion time (a) Nyquist and (b) Bode plot-Impedance.

The proposed equivalent circuit used describes the behavior of a process characterized by two time constants, namely a high-frequency (HF) time constant (CPE1−R1) and a low-frequency (LF) time constant (CPE2−R2). The low frequency data are on the right side of the Nyquist plot and higher frequency data are on the left. CPE2 is the constant phase element for the double layer capacitance of the interface at, or near, the coating/substrate interface. R2 represents the polarization resistance which is the Faradic charge transfer resistance related to electrochemical reactions in the same coating/substrate interface region [5]. It is R2 that primarily controls the corrosion resistance of the coated alloy.

The tungstate addition produces changes in the microstructure and phase contents of the coatings. Increasing the tungstate content from 0 to 6 g/l in the

electrolyte increases the thickness of the dense substrate/coating interface layer, enhances the corrosion resistance for immersion times (0.33 h) prior to corrosion, reduces the surface roughness which leads to a decrease in the COF in dry sliding wear (Fig. 4), and leads to the formation of the tungstate-containing phases WO_3 and $MgWO_4$ (see Fig. 6). All these factors, together with a reduction in porosity, leads to a harder coating with lower wear rates.

Fig. 4(b) shows that sample S4 treated with high tungstate concentrations shows a lower coefficient of friction (COF) compared with samples treated without tungstate or with lower tungstate concentrations. However, the uncoated samples exhibit the minimum COF. The lowest wear rate was produced with the highest tungstate addition. However, all PEO coated samples show a lower wear rate than the uncoated alloy, Fig. 4(a). In the pin-on-disk tests, the COF is shown to be directly dependent on the surface roughness's parameters; (Fig. 5(b)). The tungstate ions may also serve as a corrosion inhibitor and promote the formation of a passive film, which is essential for the deposition of PEO coatings on the Mg alloys
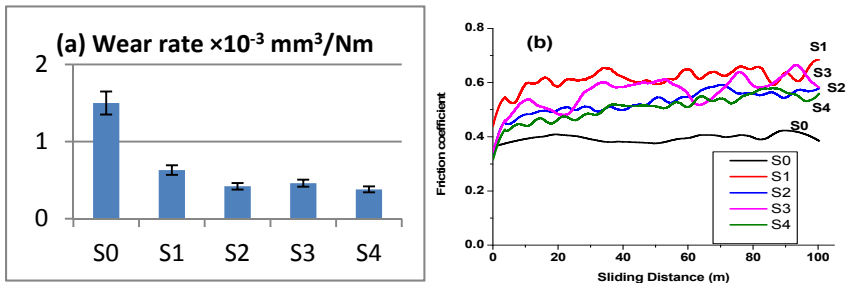

Figure 4:   (a) Wear rates and (b) coefficient of friction vs. sliding distance of the uncoated Mg alloy substrate and the oxide coatings formed using different tungstate concentrations.
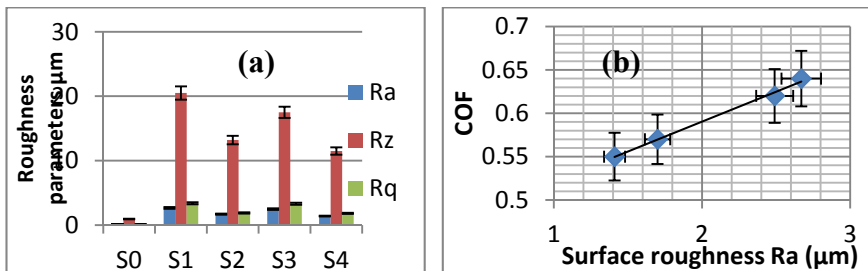

Figure 5:   (a) Roughness parameters Ra, Rz and Rq of the oxide coatings formed using different tungstate concentrations and the S0 uncoated Mg alloy substrate. (b) Coefficients of friction vs. roughness parameter Ra of the oxide coatings on AZ91D-Mg alloy substrate.
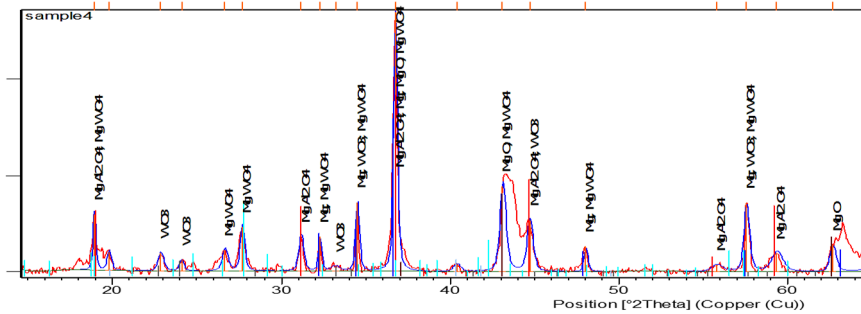
Figure 6:   XRD patterns of oxide coatings formed in $Na_2Al_2O_4$ + 1g/l KOH electrolyte with addition of 6.0 g/l Na_2WO_4 (sample S4).

3.3 Effect of current mode

The influence of current mode (unipolar U, bipolar B or hybrid H1 (unipolar followed by bipolar) and H2 (bipolar followed by unipolar)) on the corrosion and wear properties of PEO coatings formed on an AM60B magnesium alloy was investigated and are shown in Figs 7 and 8 [5]. The wear resistance was evaluated using a pin-on-disk set-up under dry conditions and a 2N applied load. PEO coating decreases the wear rate, Fig. 7(a), but also increases the COF (Fig. 7(b)). This increase in COF is related to an increase in surface roughness, Fig. 7(c). Corrosion testing was performed in a 3.5 wt% NaCl solution using a potentiodynamic polarization technique. Rp, the polarization resistance, was used as the measure of corrosion resistance. The results are summarized in Table 2 and Fig. 8.

Table 2:   Characterization of coated samples and dry sliding wear results.

S	Coating thickness (μm)	Surface roughness Rz (μm)	Level of porosity and other defects	Rp $\Omega\bullet cm^2$	COF	Wear rate $\times 10^{-4}$ mm^3/N m
U	40 to 55	44.3 ± 1.6	Porous with many microcracks	5.8E07	0.72 to 0.8	6.24 ± 2.0
B	31 to 42	31.3 ± 0.7	Low level of porosity and microcracks	8.4E08	0.55 to 0.6	1.78 ± 0.4
H1	22 to 38	34.2 ± 0.5	Low level of porosity and microcracks	4.5E09	0.55 to 0.6	4.14 ± 1.0
H2	21 to 39	37.1 ± 1.2	Intermediate level of microcracks and porosity	1.9E08	0.65 to 0.7	4.96 ± 1.2
S0	NA	2.6 ± 0.2	NA	2.8E05	0.4 to 0.5	9.0 ± 2.7

The reduction of the porosity and other defects, e.g. micro cracks, gas trapping, discontinuity between the coatings and the substrate, of the coatings, together with lower surface roughness that are produced by the B and H1 current modes compared to the U and H2 modes lead to improvement in both corrosion and wear resistance (including a decrease in COF), even though the coatings were thinner. Use of a bipolar current mode reduces number of large pancake features on the surface, thus lowering the surface roughness and COF. In the pin-on-disk tests, the COF is shown to be directly dependent on the surface roughness, Rz (Fig. 7(d)). The corrosion performance is more closely related to the protective nature of the dense oxide layer at the coating/substrate interface. In this regard, the most protective oxide is formed by using the bipolar and hybrid 1 (H1) current modes (Fig. 8).
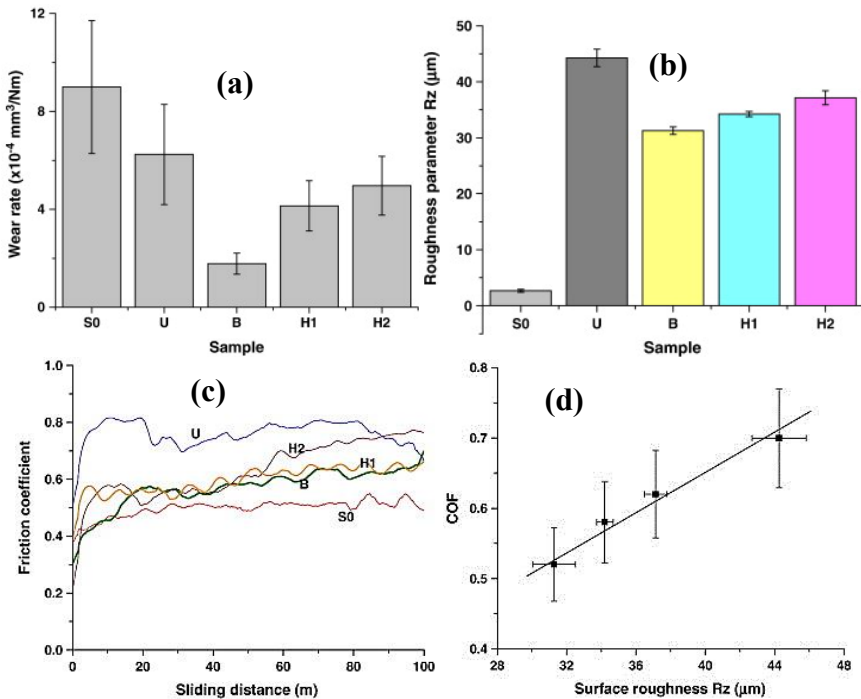

Figure 7:   Wear rate (a), roughness parameter Rz (b), coefficients of friction vs. sliding distance (c) and coefficients of friction vs. roughness parameter Rz (d) for samples U, B, H1, and H2 and the S0 uncoated AM60B Mg alloy substrate and H2 and the S0 uncoated AM60B Mg alloy substrate.
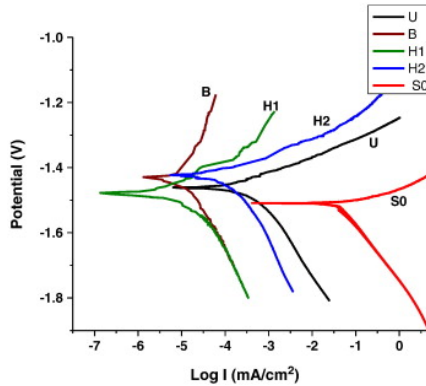
Figure 8:   Potentiodynamic polarization curves of the uncoated (S0) and coated
             AM60B alloy samples using unipolar (U1), bipolar (B) and hybrid
             (H1 and H2) current modes.

4   Conclusions

The PEO process for coating Mg alloys is strongly influenced by such
parameters as electrolyte composition and concentration, and current mode
(unipolar, bipolar and hybrid (combination of both)). Generally, these parameters
have a direct influence on the discharging behavior, porosity and microcrack
levels, roughness, phase transformations, crystallization and sintering. This, then,
affects the physical, mechanical and chemical properties of the coating. For
PEO-coated materials, the primary enhancement of the corrosion and wear
resistance comes from:

– The inner dense barrier layer, but also from the relatively dense intermediate
layer,

– The denser coatings with lower surface roughness that are produced by the
bipolar and hybrid (unipolar followed by bipolar) current modes lead to
improved corrosion resistance and tribological performance compared to those
produced using a unipolar or hybrid (bipolar followed by unipolar) current
modes.

– Each coating has a different phase composition and surface morphology due
to the effect of different electrolyte chemistry. We have shown that increases in
the $MgAl_2O_4$ spinel phase content and the tungstate-containing phases
including WO_3 and $MgWO_4$, together with a reduction in porosity, leads to
coatings with lower wear rates as well as increased corrosion resistance.

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