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Incorporation of halloysite nanotubes into forsterite surface layer during plasma electrolytic oxidation of AM50 Mg alloy

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Abstract

The increasing demand for high-performance lightweight metallic materials is driving an interest in Plasma Electrolytic Oxidation (PEO) as one of the most promising techniques for surface engineering of Mg. In order to enable smart and multifunctional performance, it can be beneficial to incorporate into ceramic PEO coatings nanocontainers to carry appropriate active and functionalising agents. *In situ* incorporation of nanocontainers is challenging since their integrity may be compromised by plasma discharge assisting coating formation. We studied incorporation of halloysite nanotubes (HNTs) as potential nanocontainers into forsterite, Mg_2SiO_4 , formed during PEO processing of AM50 alloy at the frequency range of 100-5000 Hz. Detailed analysis of the coating microstructure, chemical and phase composition carried out by Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy, Transmission Kikuchi Diffraction and X-ray Diffraction enabled evaluation of a pattern of surface temperature evolution during current pulses underpinning the PEO process. Transient analysis revealed that at pulses longer than 10^{-4} s, the surface heating becomes affected by the metal substrate acting as a heat sink. As the pulse duration approaches 10^{-3} s, raising surface temperature and increasing thermal gradients across the coating cause crystallisation of forsterite and grain growth towards the surface; this triggers thermally induced degradation and decomposition of HNTs adsorbed on the surface. In contrast, at short pulse durations (2×10^{-5} s), the energy released is insufficient to induce forsterite crystallisation and incorporated HNTs are retained in their original tubular structure. Due to the fine porosity and good structural integrity, such coatings show enhanced corrosion resistance in saline solution. Strong

correlations between surface thermodynamic conditions and evolution of coating microstructure disambiguate the fundamental mechanisms underlying incorporation of nanoparticles into growing PEO coatings, thus creating the basis for efficient design of PEO processes and development of novel smart and multifunctional coatings with potential applications in many industrial sectors.

Keywords

Plasma electrolytic oxidation; halloysite nanotube; effective temperature; corrosion; electrochemical impedance spectroscopy

1. Introduction

The increasing demand for the use of light alloys in high-performance weight-sensitive applications is often hindered by their susceptibility to environmental degradation. The urgent need to overcome this problem has boosted the development of novel treatments capable of improving the long-term corrosion resistance of these types of advanced engineering materials. Plasma electrolytic oxidation (PEO) is considered one of the most promising techniques for surface modification of light alloys, which can provide an ecologically friendly alternative to acid based anodising processes and highly toxic chromate-based treatments [1]. PEO stemmed from conventional anodising but normally utilises alkaline electrolytes and operates above the breakdown voltage of the growing oxide film. This results in the development of plasma microdischarges at the metal/electrolyte interface, where plasma-assisted chemical reactions occur, leading to the formation of chemically stable ceramic phases. PEO coatings usually possess a layered morphology comprising a barrier layer adjacent to the substrate followed by a compact nanostructured inner layer, both providing barrier corrosion resistance, and a thick (typically several tens of microns) external layer with variable porosity, which limits the ingress of corrosive agents through the coatings. PEO treatments have been widely applied to titanium [2], aluminium [2, 3] and magnesium [1] alloy substrates, with commercialised technologies emerging onto the market [4, 5].

The morphology, composition and properties of PEO coatings greatly depend on the characteristics of plasma microdischarges that are directly related to the electrical regimes used during processing (current control mode, current density, voltage magnitude, pulse shape, frequency and duty cycle). Higher voltages and current densities usually result in increased microdischarge energy which often leads to higher metal oxidation rates and therefore thicker coatings [6]. This, however, increases the surface roughness and coating porosity [7]. Decreasing the duty cycle usually increases the microdischarge ignition voltage, reduces the

population density and increases the intensity of the microdischarges [8]. This may help in refining coating morphology, with smaller dimensions of discharge craters, lower porosity and greater thickness obtained [1]. Additionally, higher frequencies provide shorter current pulse times; leading to higher rates of less intense breakdown events. This in turn reduces the coating growth rate [9] and usually results in a higher number of smaller pores in the surface morphology [10], although Cengiz [11] found the opposite trend. However, the abovementioned relationship between processing electrical parameters and the coating microstructure is only qualitative. So far, there are no quantitative methods available to determine the thermodynamic conditions within the plasma microdischarges to establish a direct link between the energy input, plasma nature, electrochemistry, microstructure and, therefore, materials properties.

Amongst the major advantages of PEO technology is the possibility of modifying the surface composition by combining substrate oxidation with incorporation of other electrolyte constituents. One of the emerging trends consists in the addition of insoluble particles to the electrolyte, which are incorporated into the surface layer through cataphoretic effects, with the aim of enhancing specific properties or promoting additional functionality. For instance, it has been shown that the coating corrosion behaviour is improved with the addition of ZrO_2 [12] or CeO_2 [13] particles, whereas the incorporation of Al_2O_3 [14], TiO_2 [15], SiC [16] and SiO_2 [17] improves mechanical properties. Lu et al. [18] revealed that the particle uptake from the electrolyte depends greatly on the electrical parameters, more specifically on the frequency of pulsed current used for the coating formation. Particle incorporation is deemed to occur via the molten pools formed at the microdischarge sites; therefore, higher pulse frequencies would usually result in a lower particle uptake, as less intense microdischarges melt smaller volumes of material on the surface. Lower frequencies are understood to increase a risk of particle

annihilation due to so-called ‘reactive incorporation’, however it is not *a priori* clear how this process would develop under the PEO treatment conditions.

Although PEO coatings can improve corrosion resistance, they usually offer passive protection, providing a physical barrier between the metal substrate and the aggressive environment. Therefore, a promising approach exists in the activation of these inert ceramic coatings by incorporation of materials with smart functionalities. The active function relies upon material’s ability to release on-demand active species as a selective response to certain triggers (e.g. time, pH and mechanical damage). Examples of this approach are provided by self-healing coatings that are capable of mitigating the corrosion attack by releasing encapsulated inhibitors when detecting electrochemical activity. This strategy has been successful in polymeric based materials and organic coatings [19, 20]. However, the active functionalisation of ceramic materials is more challenging since inorganic matrices are more rigid and inert compared to the organic ones.

Attempts to achieve this active functionalisation of PEO coatings have been previously carried out by Gnedenkov et al. [21, 22], who directly incorporated corrosion inhibitors (8-hydroxyquinoline) into the pores of PEO coatings formed on a Mg-Mn alloy through an immersion post-treatment. Although an improvement of the corrosion resistance was observed, the effect of the corrosion inhibition was partial and only lasted for a short period of time. It is probable that all of the inhibitor was released into the medium at the beginning of the corrosion process. Yang [23] developed a hybrid coating by impregnating an anodised layer on a magnesium alloy with 3-methysalicylate corrosion inhibitor and then sealing with an epoxy film, and observed a reduction of the intensity of the electrochemically active areas. Encapsulation of the active agent into nano-containers provides an alternative approach to achieve the controlled release of the inhibitors. Mohedano and Serdechnova et al. [24, 25] deposited nano-containers based on layered double hydroxides (LDH) on PEO coated AA2024

aluminium alloy followed by their intercalation with vanadate inhibitors using immersion post-treatment. It was possible to reduce considerably and control the corrosion response of the coatings, thereby achieving the total self-healing of PEO coatings on Al after external damage. However, the above work employed a two-step coating process, where the PEO treatment is applied in the first step, and the active functionalisation is carried out in the second step. A simpler but more challenging approach consists of a single-step process wherein the incorporation of nano-containers is achieved *in situ*, while the coating is being formed. Obviously, such an approach relies upon the possibility of incorporating particles from the electrolyte to the coating. Furthermore, the incorporated particles would usually suffer from superficial modifications as a result of the high temperature and pressure developed within the plasma microdischarge. From general considerations [18], the extent of modification, which defines the mode of particle incorporation – reactive or non-reactive (inert) – would depend on the nature of the particle and metallic substrate, electrolyte composition and electrical parameters of the PEO process. In the case of nano-containers, inert incorporation is essential; however, there is no clear understanding at the moment how this can be achieved under the extreme conditions developed at the sites of microdischarges that might compromise container integrity.

In the present work, halloysite nanotubes (HNTs) were selected as nano-containers that could potentially host active species. HNTs are natural clays composed of aluminosilicates and have already demonstrated utility as nano-containers for different types of species such as corrosion inhibitors [26], anti-oxidants [27] and drugs [28]. Previous studies by Sun et al. [29] revealed a partially reactive incorporation of HNTs loaded with benzotriazole, a well-known corrosion inhibitor, into PEO coatings formed on AM50 magnesium alloy, however the process still needs to be optimised to achieve the maximum HNTs uptake with non-reactive incorporation.

The main objective of this work is to evaluate the influence of frequency on the incorporation of HNTs into PEO coatings formed on AM50 magnesium alloy, thus providing insights into relationships between electrical parameters of PEO processing and conditions developed in the plasma microdischarges. Establishing this relationship will contribute decisively to the understanding of the fundamental science behind the process that is a prerequisite to be capable of manufacturing tailored materials on demand. The coatings obtained undergo detailed microstructural characterisation and preliminary evaluation of corrosion resistance. These results open the possibility for a single-step active functionalisation of PEO coatings that could expand considerably the multifunctional performance of such coatings once the nanotubes are loaded with different active species, such as corrosion inhibitors for anti-corrosion coatings; lubricants for tribological contacts or drugs for biomaterials used in biomedical implants.

2. Experimental

2.1. Materials

Samples made of a commercial AM50 (nominal composition wt. %: 4.5-5.3 Al, 0.28-0.5 Mn, 0.2 Zn, <0.05 Si, <0.004 Fe, <0.008 Cu, < 0.001Ni, Bal. Mg) magnesium alloy were used as substrates. Disks 20 mm in diameter and 5 mm thick were cut and ground with silicon carbide paper up to grade P1200 ($R_a = 0.22 \pm 0.01 \mu\text{m}$). Then, they were cleaned with water and rinsed with acetone.

A nanoclay comprising halloysite nanotubes with a diameter of 30-70 nm and a length of 1-3 μm was purchased from Sigma Aldrich. A detailed description of its morphology can be found in [30]. Na_2SiO_3 was purchased from Fisher Chemical. KOH (86.1 %) was purchased from VWR and NaF (99 %) was purchased from Alfa Aesar.

2.2. Plasma Electrolytic Oxidation

PEO coatings were obtained in an alkaline electrolyte composed of 12 g l⁻¹ Na₂SiO₃, 2 g l⁻¹ KOH, 4 g l⁻¹ NaF and 10 g l⁻¹ HNTs using an electrolyser equipped with a cylindrical stainless steel cathode, stirring and cooling system to maintain electrolyte temperature around 20° C. A 30 kW DC power supply MDX II (Advanced Energy Industries, Inc.) coupled with a SPIK2000A pulse unit (Melek GmbH) was used to provide a pulsed unipolar polarisation with the mean current density of 40 mA cm⁻² for 5 min. The duty cycle was 10% and the studied frequencies were 100, 500, 1000 and 5000 Hz. The typical electrical waveform acquired during unipolar PEO treatments can be found in [29].

Optical emission spectra (OES) of plasma discharge during the PEO process were recorded using a FloTron XHR spectrometer (Nova Fabrica Ltd, Lithuania) in the wavelength range of 300 to 800 nm with 0.5 nm resolution. The optical signal was collected via a focusing lens located at a distance of around 10 mm from the sample surface and guided to the spectrometer by an optical fibre. The collected spectra were analysed using the NIST Atomic Spectra Database [31]. Plasma electron temperature T_e was evaluated (under the assumption of a local thermodynamic equilibrium) by equation (1) [32], using intensity ratio of two spectral lines of atomic magnesium (Mg I), namely $I(1)$ at $\lambda_0(1) = 383.8$ nm and $I(2)$ at $\lambda_0(2) = 518.3$ nm [33], corresponding to electron transitions 3s3d ³D→3s3p ³P and 3s4s ³S→3s3p ³P respectively:

$$\frac{I(1)}{I(2)} = \frac{A_{mn}(1)g_m(1)\lambda_0(2)}{A_{mn}(2)g_m(2)\lambda_0(1)} e^{-\frac{E_m(2) - E_m(1)}{k_B T_e}} \quad (1)$$

Here A_{mn} is the probability of electron transition from the upper (E_m) to the lower (E_n) energy level; g_m is the statistical weight of the upper level and k_B is Boltzmann's constant.

2.3. Characterisation of PEO coatings

Surface plane and cross-sectional views of the coated specimens were analysed by scanning electron microscopy (SEM) using a FEI Magellan HR FEG-SEM equipped with a Forward Scatter Detector (FDS) and Zeiss Ultra 55 equipped with an Oxford Link attachment for Energy Dispersive X-ray Spectroscopy (EDS) microanalysis. Cross-sections in characteristic areas were prepared using an FEI Quanta 3D instrument equipped with a focused ion beam (FIB) milling facility. Selected areas were coated with platinum to prevent irradiation damage during preparation. Trenches of $\sim 40\ \mu\text{m}$ width and $\sim 30\ \mu\text{m}$ depth were milled using an accelerating voltage of 30 kV, with currents of 65 and 15 nA for rough milling. Ion currents of 5 and 0.3 nA were used for final polishing of the observed cross-sections in order to obtain good quality for imaging in an SEM at the 30° stage tilt. Electron-transparent samples for t-EBSD (Transmission Electron Backscatter Diffraction) and EDS analysis were prepared by an in situ lift out method at the areas of specific cross-section. Currents of 300 and 100 pA at 5 kV were used for final thinning (30 kV and 5 cleaning) of the lamella. Transmission Kikuchi Diffraction (TKD) [34], originally called t-EBSD [35], was performed on an FEI Magellan FEG-SEM XHR (Field Emission Gun Scanning Electron Microscopy, Extreme High Resolution) 400L equipped with a NordlysNano EBSD detector at 30 kV with a probe current of 1.6 nA. The step size for t-EBSD was 30 and 60 nm. The Kikuchi patterns were taken at 4×4 binning with an acquisition speed of 3 and 10 Hz. In order to achieve optimal spatial resolution, the EBSD measurements were performed in transmission geometry. The sample was tilted at 20° away from the EBSD detector with a working distance of 2 mm. The Kikuchi patterns were indexed using the AZtec software suite developed by Oxford Instruments [36].

Phase identification was carried out by X-ray diffraction (XRD) analysis using a Philips X'Pert-MPD instrument operated in the Bragg-Brentano geometry ($\text{Cu K}\alpha = 1.54056\ \text{\AA}$). The

XRD spectra were taken in the range of 2θ from 20° to 80° with a step size of 0.02° and a dwell time of 5 s per step. The peak indexing was carried out using the ICDD PDF4+ database and the X'pert High Score software.

Quantitative image analysis was carried out on minimum two SEM micrographs taken at $500\times$ magnification ($600\times 515\ \mu\text{m}^2$) at arbitrarily locations using ImageJ software. To quantify the coating porosity, micrographs were transformed into a 8-bit greyscale and a median filter of 2 pixel ratio was applied to smooth and reduce the random noise. An automated segmentation was carried out to perform the quantification of the porosity in order to avoid user bias and ensure reproducibility.

A Laser Scanning Confocal Microscope VK-200 Series was used to obtain the surface topographic maps at $150\times$ magnification ($265\times 200\ \mu\text{m}^2$). A VK Analyser software was used to evaluate the surface roughness of the coatings by applying an average filter of 3×3 pixels.

2.4. Corrosion tests

Electrochemical corrosion evaluation of the PEO coatings was carried out in a naturally aerated aqueous solution of 3.5 wt. % NaCl (pH = 6.5) at $23\ ^\circ\text{C}$. The open circuit potential was monitored for 1h followed by Electrochemical Impedance Spectroscopy (EIS) to evaluate the coating corrosion resistance. The measurements were carried out using a Solartron computer-controlled potentiostat using a three-electrode cell. The specimen with an exposed surface area of $1\ \text{cm}^2$ acted as the working electrode and a platinum and a silver–silver chloride (Ag/AgCl) ($0.210\ \text{V vs. SHE}$) electrodes were used as the counter and the reference electrode, respectively. A 10 mV RMS sinusoidal perturbation was applied in the frequency range of 10 kHz to 0.01 Hz. All measurements were duplicated to ensure reproducibility. The impedance data were

fitted using ZView software (Solartron Analytical) with a <10% error for each element and η^2 values of <0.02.

3. Results and discussion

3.1. Characteristics of the PEO process

Figure 1a depicts the typical voltage-time response during the PEO treatment of AM50 magnesium alloy at the studied frequencies. All curves follow a similar trend and present three different stages [7, 37]. In Stage I, the voltage increases rapidly and small gas bubbles are formed on the metal surface, which indicates that the magnesium substrate is being passivated in alkaline media. During Stage II, the voltage keeps increasing, but at a lower rate compared to the previous stage. The coating growth at this stage is accompanied with a great number of small white microdischarges and intense gas evolution. In Stage III, the voltage increase slows down, with absolute values remaining at ~450 V, indicating low coating growth rates. During this last stage, the number of microdischarges decreases and they increase in size, changing colour from white to orange. Optical emission from plasma at this stage (Figure 1b) is dominated by the spectral line of Na (589.5 nm), with the duplex of K (765-770 nm) also being relatively strong and weak peaks of OH (around 310 nm), Mg (383.8, 448.1, 518.3 nm), Al (358.7 nm) and H (656.3 nm) bringing rather minor contributions to the spectrum. The main difference between all treatments is the relative duration of Stages II and III. Increasing processing pulse frequency results in an extension of Stage II, where there is a high number of small microdischarges and reduction of Stage III, characterised by a smaller number of more intense localised microdischarges. The transition from Stage II and Stage III depends greatly on the coating thickness; therefore, the longer Stage II observed at higher frequencies is probably related to the lower growth rates compared to the coatings produced at lower frequency, which leads to a longer transition to Stage III. In this final stage, the average voltage

at high frequency (5000 Hz) climbs up at higher rates, that is why all the coatings end up with similar thicknesses. Therefore, the coating formed at 5000 Hz grew mainly under the conditions corresponding to Stage II, while at 100 Hz the main coating growth occurred during Stage III. Despite that, plasma electron temperature remained in the same range of $(2.5-3.6) \times 10^3$ K, which is generally consistent with the lower range estimates of $T_e \sim 3.3 \times 10^3$ K made by Hussein, et al. [33] for the pulsed unipolar PEO processing of AJ62 Mg alloy at 0.65 mA cm^{-2} current density, 2 kHz pulse frequency and 80% duty cycle. This range was attributed to small superficial discharges termed Type A and C in [38], however no evidence of the large powerful discharges of Type B, which were observed at the final stages of coating formation in the above two works and characterised by a higher range of $T_e \sim (4-7) \times 10^3$ K, could be found under the conditions of the present study, which is probably due to lower current density (40 mA cm^{-2}) and pulse duty cycle (10%) employed.

3.2. Morphological features of HNT-containing PEO coatings

The micrographs in Figures 2 and 3 show respectively the surface plane and cross-sectional views of the PEO coatings formed on AM50 magnesium alloy at 100, 500, 1000 and 5000 Hz. All coatings exhibit a crater-like morphology formed as a consequence of gas evolution during eruption of the molten material induced by high temperatures developed at the sites of local microdischarges and followed by rapid solidification due to cooling by the electrolyte once the discharge is extinguished [28].

All coatings present a similar thickness of $14.4 \pm 0.9 \text{ }\mu\text{m}$ and a three-layer structure consisting of the inner barrier layer with thickness of $0.7 \pm 0.1 \text{ }\mu\text{m}$, an intermediate microporous layer and the outer macroporous layer, both with variable thicknesses. A strong influence of the current pulse frequency on the resulting coating porosity can be clearly observed in both surface plane (Figure 2) and cross-sectional images (Figure 3), which is related to the entrapment of evolved

gas bubbles within the molten metal [39]. An increase in the pulse frequency causes the thickness of the intermediate layer to increase and that of the macroporous layer to decrease, which results in coatings with refined porosity. Based on SEM observation of the open porosity (Figure 4), the net area fraction and density of pores increase from 10.1 ± 1.9 to $16.4 \pm 3.0\%$ and from 5789 ± 647 to 19014 ± 288 pores mm^{-2} respectively, when increasing the pulse frequency from 100 to 5000 Hz. However, the pore size distribution follows the opposite trend, decreasing with increased frequency. Figure 4c shows that the fraction of pores above $70 \mu\text{m}^2$ decreases and that below $10 \mu\text{m}^2$ increases significantly when increasing the pulse frequency. Therefore, higher frequencies lead to coatings that are more porous albeit having a smaller pore size. This is associated to a longer Stage II (Figure 1) during the processing, which is characterised by higher density of short lifetime and less intense microdischarges [8]. Hwang et al. [40] evaluated the influence of increasing frequency on the morphology of PEO coatings formed on a Mg-Al alloy using a silicate based electrolyte and observed a comparable trend.

To provide a deeper insight into the influence of discharge duration on the coating morphology, 3D optical images of the coating surface presented in Figure 5 were used. All coatings show alternations of peaks, valleys and pores, but with clear differences in their distribution, shape and size. The coating produced at 100 Hz (Figure 5a) shows the most heterogeneous surface topology. It presents a rocky appearance where most of the peaks are agglomerated, reaching greater heights compared to the other specimens, although flat areas are also observable. Longer lifetime of microdischarges promotes flow of molten material that tends to agglomerate due to surface tension effects, which results in the formation of these protuberances. This is evident in the cross-sectional micrograph (Figure 3a) which shows a thicker outer macroporous layer with large transversal pores and a reduced intermediate microporous layer. Corresponding roughness values (S_a and S_z , Figure 5) confirmed the visual observation of the coatings, which is in accordance with studies of Mann et al. [41]. When increasing the

frequency to 500 and 1000 Hz, that is reducing pulse time, more uniform microstructures are formed (Figure 5b and c). The number of protuberances with a shorter height (orange-red areas) increases covering most of the coating surface. A decrease in the pore size is evident, although the spatial distribution of pores remains relatively homogeneous. Cross-sectional observations of these coatings (Figure 3b-c) reveal the presence of monolithic phases with low porosity combined with areas containing macroporosity. The coating produced at 5000 Hz (Figure 5d) shows a uniform microstructure with a relatively flat surface where the highest peaks or protuberances are homogeneously distributed along the surface; the pores are finely scattered, covering most of the surface. This can be correlated with the cross-sectional images of the coating (Figure 3d), where a high number of homogeneously distributed pores can be observed along the thick intermediate layer.

3.3. Compositional features of HNT-containing PEO coatings

Results of XRD analysis presented in Figure 6 indicate the coatings are formed of α - Mg_2SiO_4 (forsterite). Some peaks from the Mg alloy substrate can also be observed due to X-rays penetrating through the relatively thin and porous surface layers. It is worth mentioning that no MgO was identified; this compound is usually formed in coatings processed under pulsed bipolar and alternating current conditions while Mg_2SiO_4 is preferentially formed under unipolar conditions [39]. Magnesia is formed by direct oxidation of the metallic substrate and Mg_2SiO_4 results from co-deposition of electrolyte components [39]. When increasing the pulse frequency, the coating crystallinity decreases, as can be deduced from the reduced intensity of diffraction peaks and development of the broad amorphous area at low diffraction angles in the pattern of the coating formed at 5000 Hz. This indicates the energy input provided by individual microdischarges at high frequencies becomes insufficient for crystallisation of amorphous phases in the coating matrix into Mg_2SiO_4 . This is consistent with results obtained by Rapheal

et al. [42], who observed a direct relationship between crystallinity and applied current density within the range of 30 to 120 mA cm⁻² for PEO coatings formed on AM50 magnesium alloy in a phosphate based electrolyte.

It is important to clarify that characteristic peaks of halloysite nanotubes at 2θ values of 21° and 31° could not be observed in the XRD spectra, probably due to relatively low amounts of HNTs incorporated in the coatings. Nevertheless, the presence of HNTs within the coatings is evident in Figure 7, from which it is also clear that the morphology of incorporated nanotubes depends strongly on the pulse frequency. The coating formed at 100 Hz (Figure 7a-b) shows agglomerated particles composed mainly of Si, Al and O (the main components of HNTs) but without tubular morphology in the outer part. Only a few particles identified retained the tubular shape and the others were probably thermally decomposed during relatively long lasting microdischarge events and then oxidised; therefore, the incorporation of HNTs was mainly reactive. In the case of PEO treatments at 500 and 1000 Hz, the HNTs incorporation was partially reactive since both agglomerated particles and nanotubes were observed (Figure 7c-f). When increasing the frequency up to 5000 Hz, the relative amount of HNTs with tubular morphology within the coating increased considerably, as can be clearly observed in Figure 7h. In this case, the HNTs incorporation to the coating was non-reactive.

The area EDS analysis of the coating surface (Table 1) shows that the coatings are mainly composed of Mg, Si and O, which is generally consistent with the results of XRD analysis (Figure 6), indicating the presence of the Mg₂SiO₄ phase. The Mg:Si ratio in the crystalline phase is 2:1; however, the total amount of Si determined by EDS exceeds this relationship. The difference, ΔSi is in the similar range as the total amount of Al present in the outer layer of the coating; this could possibly be attributed to HNTs which have a Si:Al ratio of 1:1. All coatings also show F, and small amounts of Na and K. It is possible to observe some compositional

differences depending on the pulse frequency used during the coating processing. When decreasing the pulse frequency from 5000 to 100 Hz, there is an increase in amount of Al from 1.3 to 1.5 at. % and in the ΔSi from -1.1 to 2.9 at. %, respectively. The negative value of ΔSi in the coating produced at 5000 Hz is probably due to the presence of amorphous non-stoichiometric phases (Figure 6). This indicates that there is a higher HNTs uptake when decreasing the pulse frequency, which is in accordance with the work by Lu et al. [18]. However, as shown in Figure 7, at low frequencies, HNTs are incorporated in a reactive way, losing their original morphology, which would compromise their performance as active substance carriers.

There are also some compositional differences in the inner layers of the coatings. Figure 3 shows the results of point EDS analysis across the coating cross-section, divided into six different locations from the inner part of the coating adjacent to the substrate (1) to the outer, nearest to the surface region (6). All samples contain small amounts of Al, being slightly greater at the inner part of the coatings which is related to the incorporation of this element from the alloy which contains ~ 5 wt. % of Al in its composition. Additionally, the ΔSi also tends to increase as the distance from the substrate increases. This suggests HNTs have been incorporated mostly in the outer parts of the coatings, which is consistent with earlier observations [29].

The fluorine content on the coating surface (Table 1) is in the range of 5 to 8 at. %. This is due to NaF being introduced in the electrolyte since F^- anions are known to facilitate the passivation of magnesium substrates [43], which promotes formation of coatings with improved mechanical properties and corrosion resistance [44]. It is worth mentioning that the amount of F within the coating increases with the pulse frequency. Probably, the higher population density of microdischarges within the coating promotes the access of F^- ions from the electrolyte to the

coating. Additionally, it can be observed in Figure 3 that the fluorine content is higher in the inner parts of the coatings. This is more evident in the coatings synthesised at lower frequencies, where higher pulse durations promote F^- migration towards the metal surface and its transport in the ceramic surface layer.

3.4. Further evidence of HNTs incorporation from detailed microscopic analysis

Figure 8 shows agglomerations of HNTs on the surface of the AM50 Mg alloy with PEO coating formed at the frequency of 5000 Hz. A FIB section across the regions with HNTs 1 and 2 (marked by the dashed line in Figure 8a) reveals a presence of nanotubes with the tubular shape inside the coating pore (Figures 8c-f). Due to the similar composition, the contrast difference between the HNTs and the coating matrix is low, which makes the observation of HNTs within the coating difficult. However, the precise location of the FIB section reveals the congruent shape of the nanotubes passing through the coating material into the pore. Figures 8e-f show the detail of the nanotube corresponding to the region 1 marked in Figure 8b. A slight difference in contrast of the nanotube in the backscattered electron mode in Figure 8f could be due to a significantly smaller volume of the material within the nanotube features. A similar effect can be observed on the inner wall of the pore. The presence of the nanotubes inside the pore of the coating formed at frequency 5000 Hz suggests the possibility of their non-reactive incorporation within the whole thickness of the coating.

An electron-transparent sample was prepared as a cross-section of the PEO coating formed at frequency 100 Hz to study the coating crystallinity and elemental distribution. TKD and EDS analysis was performed across the whole thickness of the coating. The electron micrograph (FSD) in Figure 9a confirms clearly the presence of the inner barrier layer, intermediate microporous layer and a presence of the macropores. The latter appears as occluded porosity with pore size of the order of tens of microns. However, the study of PEO coatings on Ti using

X-ray computed tomography revealed that the features similar to those observed on the SEM cross-sections are actually connected to the coating surface [45]. In addition, a layer cladding the walls of the macropore appears due to the artefacts associated with re-deposition of the sputtered material during FIB milling. A band contrast image in Figure 9a shows a crystalline structure in the outer part of the coating covered with a thin amorphous layer on the surface. The resolved grain size was in the range of ~ 100 nm to ~ 3 μ m. No crystalline structure was detected in the inner part of the coating. The spatial resolution of the TKD technique in optimal conditions is ~ 10 nm [36]; therefore, the ordered structure on a nanometre scale would not be detected. The phase map of the same region shows the presence of orthorhombic phase α - Mg_2SiO_4 ($a = 4.7520$ Å, $b = 10.1920$ Å, $c = 5.9780$ Å and $\alpha = \beta = \gamma = 90^\circ$) [46] within the coating and Mg in the substrate. The matched Kikuchi patterns (EBSPs) for Mg_2SiO_4 in Figure 9b confirm that the modelled phase provides a good fit. Such a result is in agreement with XRD analysis (Figure 6). EDS elemental maps show a relatively uniform distribution of aluminium and magnesium with a slight depletion of Mg on the grain boundaries and in the inner amorphous part. Distributions of oxygen and silicon generally follow a similar trend, although the latter is not present in the barrier layer at the interface with Mg alloy. Instead, this layer is enriched in fluorine which is present mainly within the amorphous constituent of the inner layer, with its content decreasing through the crystalline part. The lower signal at the bottom right corner of the EDS maps is due to the SEM configuration and shadowing of the EDS detector.

Detailed EDS elemental maps together with the electron (FSD) and band contrast images as well as the grain orientation map from the crystalline layer are shown in Figure 9b. In relation to TKD band contrast image, magnesium, oxygen and silicon are depleted in the amorphous areas between the grains where the increased concentration of fluorine was detected. The Si

map shows a higher contrast in the area of bigger grains, whereas Al is distributed relatively uniformly.

Figure 10a shows the FSD-SEM micrograph of the electron transparent specimen prepared in the area of the cross-section (shown in Figure 8) of the PEO coating formed at 5000 Hz. The electron transparent specimen revealed band-like areas within the coating (marked by arrows). The contrast in these areas clearly differs from that representing pores. Considering the dimensions and distributions, the features are most likely to represent clusters of nanotubes incorporated into the coating structure. Assuming the HTNs were incorporated in the non-reactive way, these features would correspond to their cross-sectional views; i.e. tubes with diameter of 30 to 70 nm. Such dimensions, with consideration of the thin wall of the nanotubes, are below the detection limit of the EDS analysis. The HR EDS elemental mapping from the central area of the coating is shown in Figure 10b. Magnesium is depleted in the area of the dark band and fluorine enriched in the vicinity of this area. Oxygen is distributed relatively uniformly. Aluminium and silicon maps show locally increased concentrations that could be related to the HNTs clusters. The fluorine map across the whole section (not shown) revealed a presence of fluorine across the whole coating thickness, with an increased concentration in the inner part. The detailed SEM micrograph of the coating/Mg alloy interface is presented in Figure 10c together with elemental maps of Mg, F, O, Al, Si and Zn. The fluorine map shows an enriched layer of approximately 1 μm thick near the coating/alloy interface, where the concentration of both oxygen and silicon is decreased. The EDS analysis in the high magnification revealed zinc enrichment beneath the coating. A similar effect has been observed previously during formation of barrier anodic films on Mg alloys [47, 48]. No crystalline structure was detected within the coating formed at 5000 Hz by TKD analysis. This is in agreement with the results of XRD analysis (Figure 6) where only minor peaks of Mg_2SiO_4 were identified.

3.5. Thermodynamic conditions influencing the mode of HNTs incorporation

It is clear that, in general, the mode of HNTs incorporation into PEO coatings depends upon thermodynamic conditions developed at the surface. However, identifying the key influencing parameters is not a trivial task. The particle incorporation mechanism is quite complex, comprising a combination of different phenomena, including field assisted electrophoretic transport in the electrolyte, adsorption on the electrode surface, entrapment by the molten material created in the discharge zone and subsequent thermal-chemical interaction with it [49-51]. The extent of reactive transformation experienced by HNTs during incorporation depends upon the energy dissipated in the microdischarge event, which in the case of the galvanostatic regime is mainly determined by the duration of the current pulse. This energy is then consumed in heating up the particle, together with the adjacent volumes of the coating material, possible phase transformations and chemical reactions in the system (the latter however could both consume and release energy). Although a quantitative evaluation of this non-equilibrium multiphysics process with many unknowns is quite challenging, for the studied system some inferences can be made based on qualitative evidence of structural transformations occurring in the coating. Assuming the transformations are solid-state isobaric processes allows us to operate in terms of ‘effective temperature’, T_{eff} , which correlates the energy released under non-equilibrium conditions of PEO treatment to the actual temperature that would cause similar structural and phase transformations in the surface layer at equilibrium. A similar approach has been previously adopted by Lee et al. in their analysis of discharge temperature during PEO treatment of AZ91Mg alloy [52].

3.5.1. Empirical framework for estimation of the effective temperature

Yuan [53] studied the thermal stability of HNTs at different temperatures and observed that below 400 °C (673 K) HNTs remain unchanged; between 600 and 800 °C (873 and 1073 K)

they are partially dehydroxylated and the tubular morphology becomes partially modified; at 900 °C (1173 K) the tubular morphology is significantly compromised; and above 1000 °C (1273 K) the 3D structures collapse, leaving behind amorphous SiO₂ and Al₂O₃ compounds. This provides an empirical reference framework for estimation of thermodynamic conditions developed on the surface under the influence of a plasma discharge. These conditions can be correlated to the mode of HNTs incorporation and verified by the crystallinity of phases formed in the coating matrix. Thus in the coating synthesised at 100 Hz, the energy released in microdischarges was likely to be sufficient to heat adjacent material to T_{eff} of at least 1000 °C (1273 K), as deduced from the reactive incorporation of HNT. Moreover, the coating matrix produced by this treatment contained mostly crystalline α -Mg₂SiO₄ which does not have polymorphs up to its melting point of $T_m = 1890$ °C (2163 K) up to pressures of 10 MPa [54]. Considering that surface films formed at homologous temperatures below $0.3T_m$ are usually amorphous, whereas their intense re-crystallisation and grain growth commence at about $0.5T_m$, [55], effective temperatures developed at this frequency in the discharge affected zones of the surface layer can be estimated to be in the region of 950 °C (1223 K), which is consistent with those derived based on observations of structural changes in HNT. In the case of PEO treatment at 5000 Hz, the coating matrix does not present crystalline Mg₂SiO₄, suggesting the energy released during discharge was insufficient to heat the matter above T_{eff} of about 570 °C (843 K). At the same time, the non-reactive incorporation HNTs indicates that the effective temperature was possibly below 600 to 800 °C (873 to 1073 K) required for dehydroxilation of HNT, and certainly less than 900 °C (1173 K) required for separation of HNTs into its forming elements. The fact that the disappearance of tubular structures associated with HNTs commences at intermediate frequencies simultaneously with crystallisation of Mg₂SO₄ of the coating matrix implies T_{eff} in the range of 800 to 900 °C (1073 to 1173 K) could only be achieved at longer pulse durations, i.e. 0.1 to 0.2 ms.

3.5.2. Temperature transient analysis and substrate effect on the coating heating rate

The above estimates of T_{eff} are presented in Figure 11a from which it follows that the surface temperature increases rather quickly during the first 100 μs of current pulse, whereas beyond this period, the heating rate drops dramatically. In the absence of Type B discharges [33], the main driving force for the surface heating is provided by the superficial discharges of Type A and C that can be considered an external heating source with temperature T_e . According to the Newton's cooling law, the relative rate of temperature change in the surface layer will exponentially decay while the temperature difference between T_{eff} and T_e decreases with time t [56]:

$$\frac{T_{\text{eff}}(t) - T_e}{T_o - T_e} = e^{-\frac{t}{\tau}} \quad (2)$$

Here T_o is the initial surface temperature which can be accepted equal to that of the electrolyte and τ is the thermal time constant which depends upon both thermophysical properties of the material (the ratio of specific heat capacity to thermal conductivity, c_p/κ) and the scale of the system (mass and characteristic length product, $m \times l$). The analysis of data in Figure 11a reveals there are indeed two relaxation processes described by distinct time constants, $\tau_1 \sim (1.4 \text{ to } 2.0) \times 10^{-5} \text{ s}$ and $\tau_2 \sim (0.5 \text{ to } 1) \times 10^{-2} \text{ s}$, involved in the heating of the PEO coating (Figure 11b). Such a large difference between them implies that after about 10^{-4} s , the scale of the heat transfer system ($m \times l$) increases dramatically, which means the metal substrate acts as a heat sink, thus hindering the heating rate of the surface layer. This would be likely to lead to the situation when the temperature at the surface raises faster than at the interface, resulting in increasing temperature gradient across the coating. At some stage, this may also become contributed by the radiative heat exchange, which is not accounted for in Eq (2), but this effect appears to be confined by the outmost region of the coating as deduced from its cross-sectional microstructure. Since HNT incorporation starts from adsorption on the surface and its mobility

is limited by the relatively large longitudinal dimension, the temperature at the surface appears to be critically important, however the above lumped thermal analysis is not spatially resolved to reveal it.

3.5.3. Temperature distribution across PEO coating

Essential insights into temperature distribution across the PEO coating can be gained from careful microstructural examination of TKD images presented in Figure 9a. The microstructure of the coating formed at 100 Hz shows a clear evidence of crystallisation and grain growth towards the surface which is consistent with the main assumption of surface heating by an external source made in Section 3.5.2. Regression analysis (Figure 11c) suggests that the average size D of Mg_2SiO_4 grains increases with the distance from the interface x , following an exponential equation (3):

$$D = a_1 \cdot e^{b_1 \cdot x}, \quad (3)$$

with $a_1 = 5.34 \times 10^{-3}$ and $b_1 = 0.441$ for both D and x expressed in microns. A relatively high scatter in the outer region may be due to a smaller fraction of larger grains available and a relatively short time of exposure to the high temperature, resulting in only partial annihilation of smaller grains. Nevertheless, this trend is in agreement with general theory of grain boundary mobility stipulating exponential dependence of grain size on temperature. S. Ramesh, et al. [57] reported evolution of grain size in forsterite ceramics in the range of sintering temperatures from 1200 to 1500 °C (1473 to 1773 K). For the non-heat treated sample series, their data also appear to follow an exponential dependency (4):

$$D = a_2 \cdot e^{b_2 \cdot T}, \quad (4)$$

with $a_2 = 1.6 \times 10^{-3}$, $b_2 = 4.3 \times 10^{-3}$ and the coefficient of paired correlation $R^2 = 0.9$. Equalling (3) to (4) and taking logarithms at both sides yields equation (5) to estimate the distribution of T_{eff} across the coating thickness:

$$T_{\text{eff}} = \frac{\ln \frac{a_1}{a_2}}{b_2} + \frac{b_1}{b_2} x = 280 + 103 \cdot x \quad (5)$$

Substitution of regression coefficients with respective numerical values provides estimates of T_{eff} at the coating surface at about 1543 to 1583 K (1270 to 1310 °C), which is in a good agreement with the evidence of HNTs decomposition observed on the surface of this coating. Furthermore, the temperature gradient of about 10^2 K/ μm provides credible demarcation of the structural zones in the coating according to homologous temperatures, as well as indicates that the inner coating region beneath the macroporous band is formed at near to ambient effective temperatures (the latter however may be affected by fluorine stabilising the amorphous phase, as discussed in the following Section 3.5.4, which would lead to the skewed grain size distribution). These findings indicate that the reactive character of HNT incorporation at lower frequencies is thermally rather than chemically driven, i.e. the nanotubes are likely to first decompose due to sufficiently long residence at high enough temperatures developed on the coating surface and then chemically interact with the main coating material. This conjecture appears to be plausible considering similarities in chemical composition of HNT and forsterite and associated difficulties in chemical discrimination between these coating constituents discussed in Section 3.4.

3.5.4. On the significance of possible kinetic limitations

Although the above analysis shows that the crystallinity of the studied PEO coatings can be generally related to the surface temperature determined by the duration of the current pulses,

some factors may affect the kinetics of forsterite crystallisation thereby influencing the estimates of the temperature distribution across the coating. In particular, the presence of fluorine is known to promote amorphous structure in PEO coatings [58]. Higher surface temperatures developed at lower frequencies would promote transport of fluorine species towards the coating/substrate interface. A faster migration of fluorine compared to oxygen has been reported during formation of anodic films on Mg alloys from water containing organic electrolytes, with fluorine incorporated preferentially within the inner layer of the film [47, 48]. Following this, it can be speculated that the surface layer formed during Stage I was amorphous with an increased content of fluorine, and as the coating thickness increased, the fluorine species migrated inwards leaving behind a layer depleted in fluorine, where crystalline Mg_2SiO_4 could be formed. An additional migration of fluorine from the electrolyte through the crystalline structure probably occurred along the grain boundaries, promoting coating formation at the metal/oxide interface. This may explain a relatively large thickness of amorphous band observed in the inner region of the coating formed at 100 Hz and a seemingly delayed appearance of crystallinity compared to the estimate of temperature distribution across that coating (Figure 11c). However the present evidence is insufficient to judge whether the forsterite crystallisation in the middle region of the coating was hindered by the presence of fluorine or the temperature was indeed too low to trigger crystallisation.

3.6. Corrosion resistance of HNT-containing PEO coatings

Figure 12 shows the evolution of OCP values of PEO coated Mg alloy samples with the time of immersion in 3.5 wt. % NaCl solution, which provides thermodynamic information related to the equilibrium states of the studied materials as well as transitions between states (passive or active behaviour) [59], and the surface appearance after the corrosion test. In general terms, all coatings show OCP values between -1.60 and -1.40V (vs. Ag/AgCl) for all immersion times,

and they remain relatively constant through the entire experiment, which is a sign of steady state corrosion. However, some differences between the coatings are identified. The sample treated at 100Hz after 2 hours of immersion, shows a decrease in the OCP value from -1.45V to -1.52V (*vs.* Ag/AgCl) (Figure 12a). This shift towards more negative values is related to the degradation of the ceramic layer as a consequence of electrolyte penetration through the coating, promoting electrochemical activity at the coating-substrate interface. After 1000s, the OCP achieves a steady value indicative of an equilibrium state. The coatings produced at 500 and 1000Hz show relatively stable OCP values after 2h of immersion ($\sim$ -1.57 V *vs.* Ag/AgCl), which suggests that both coatings undergo a steady-state corrosion too. The specimen processed at 5000Hz shows higher values of OCP during the first 1000s of immersion (-1.40V *vs.* Ag/AgCl) compared to the other coatings, which can potentially indicate a higher corrosion resistance. During the first $\sim$ 750s the OCP values decrease constantly which indicates a possibility of electrolyte access to the substrate through the coating and corrosion degradation of magnesium, which results in the precipitation of corrosion products at the coating/substrate interface that can provide partial protection. After $\sim$ 750s, the OCP decreases drastically to -1.55V and recovers for a short period of time before finally decreasing again after $\sim$ 1350s. These fluctuations are associated to the dissolution and re-precipitation of the corrosion products. When the surface is covered by a compact layer of corrosion products that impede further advance of corrosion, the OCP increases, while these corrosion products are dissolved, the electrolyte has direct access to the substrate leading to a shift towards lower OCP values [29, 37]. At longer immersion times, 24 to 72h, all coatings show a stable corrosion behaviour with OCP values in the range of -1.57 and -1.55V *vs.* Ag/AgCl (Figure 12 b-d). The slight fluctuations of $\pm$ 0.02V are also related to the dissolution-precipitation of corrosion products. It is worth mentioning that for all immersion times the sample treated at 5000Hz presents slightly higher OCP values with smaller deviations, signifying its superior corrosion resistance. This is

probably related to the change in the coating morphology with increasing pulse frequency. The presence of a higher number of smaller pores in the coatings processed at higher pulse frequency obstructs the electrolyte access through the coating since the path to the substrate becomes more tortuous compared to that in the coatings with coarser interconnected porosity.

Figure 13 shows the EIS response of the studied coatings up to 72h of immersion in a 3.5 wt. % aqueous solution of NaCl. Nyquist plots of all coatings present a similar behaviour comprising a capacitive loop at medium frequencies (10^2 - 10^3 Hz) and an inductive loop at low frequencies (10^{-2} - 10^{-1} Hz). The capacitive loop is associated to the response of the ceramic PEO coating. The inductive behaviour in the impedance response of magnesium-based materials has been disregarded by many authors because of large data scattering due to non-stationary behaviour of magnesium at low frequencies. However, neglecting this inductive behaviour may result in an underestimation of the magnesium corrosion rate [60-62]. The inductive loop is ascribed to kinetic effects associated with adsorption-desorption behaviour of species such as atomic H, Cl^- , $\text{Mg}(\text{OH})_{2\text{ads}}$ and $\text{Mg}(\text{OH})_{\text{ads}}^+$ at the metal surface [14, 63, 64] responsible for pitting corrosion initiation [37, 65-67].

The experimental data was fitted (Table 2) to the equivalent circuit shown in Figure 13e, where R_s represents the resistance of the electrolyte; R_c and CPE_c account for the resistance and capacitive behaviour of the coating and L and R_2 represent the inductive loop [29, 68]. In order to account for the heterogeneities in the surface layers, constant phase elements (CPE) were used instead of ideal capacitors. All the studied materials show a steady decrease in corrosion resistance as deduced from the smaller diameter of the capacitive loop when increasing the immersion time from 2 to 72h. This is mainly associated with electrochemical dissolution of the magnesium substrate as a consequence of the electrolyte penetration through the pores of the coatings. Regarding the inductive loop it is possible to observe in Table 2 that L values tend to

decrease when increasing the immersion time for all the studied materials [14]. This can be explained by the fact that as the immersion time increases, Mg^{2+} ions formed during the anodic corrosion reaction tend to precipitate at the substrate/coating interface in the form of $Mg(OH)_2$ corrosion products that inhibit partially the advance of pitting corrosion phenomena that are often associated with inductive behaviour.

The impedance modulus at low frequencies (e.g. 0.1 Hz) provides a general estimation of the corrosion resistance, the higher the modulus, the better the corrosion resistance is. Figure 14 compares $|Z|_{0.1Hz}$ as a function of immersion time for different coatings, showing a direct relationship between coating morphology and the corrosion response [69]. At short immersion times (up to 24 h) the corrosion resistance of the coatings is considerably improved when increasing the processing frequency from 100 to 5000Hz. This improvement is mainly attributed to the change of the coatings morphology. The presence of a higher number of smaller pores in specimens processed at higher frequencies hampers the penetration of the aggressive electrolyte species through the coating since the access path for the electrolyte is impeded compared to the coatings with coarser interconnected porosity formed at low frequencies. This is consistent with the surface appearance of the specimens after 72h of immersion (Figure 12e), where a clear reduction in the number of pits is observed as the frequency increases. However, such improvement is appreciable only at short immersion times (< 24h), being negligible at longer immersion times (> 50h), when the electrolyte eventually reaches the substrate. This means that the refinement of the coating morphology alone is not sufficient for long-term corrosion protection by PEO coatings.

The best corrosion response was observed for the sample treated at 5000Hz. It is worth mentioning that this treatment provided the coating with a higher amount of HNT incorporated in a non-reactive form. However, the presence of HNT on its own does not positively or

negatively affect the corrosion performance of PEO coatings. The improvement in the corrosion resistance is mainly associated to the morphological refinement of the coating matrix. Therefore, these results provide a promising stepping stone on the way to achieving the active functionalisation of PEO coatings by loading HNT with active compounds. The high versatility of HNT widens considerably the applicability of PEO coatings; for instance, the encapsulation of corrosion inhibitors into HNT would allow the formation of self-healing coatings, proving long-term corrosion resistance.

4. Conclusions

The research reported here studied the incorporation of halloysite nanotubes as potential means of introducing nanocontainers into the surface layer of forsterite during PEO treatment of AM50 magnesium alloy in a silicate-based electrolyte at unipolar pulse frequencies ranging from 100 to 5000 Hz and resulted in the following conclusions:

- Although the pulse frequency affected the transition to the discharge stage during the PEO treatment, this did not have significant influence on either the final voltage or coating thickness. However, the frequency affected the coating morphology and crystallinity so that the layers grown predominantly under sparking conditions, at lower frequencies (e.g. 100 Hz), were crystalline and exhibited a coarser morphology compared to the amorphous coatings synthesised at 5000 Hz, where sparking was developed only during the final minute of processing.
- A correlation was observed between the crystallinity of the forsterite matrix and the mode of HNTs incorporation, which was linked to the thermodynamic conditions on the surface provided by the plasma discharge. At lower pulse frequencies (100 Hz), the effective surface

temperature was estimated to be well above 950 °C which is sufficient to promote recrystallisation and grain growth in forsterite as well as trigger reactive incorporation of HNTs into coatings. This suggested the reactive incorporation is likely to be thermally rather than chemically driven. At higher frequencies (5000 Hz), the energy released ($T_{\text{eff}} \sim 570$ °C) was insufficient to promote crystallisation and allowed the non-reactive incorporation of HNTs that retained their tubular structure.

- The temperature transient analysis revealed two relaxation processes involved in the surface heating by plasma discharges differentiating the initial propagation of the heat flux through the oxide layer from the later stages ($>10^{-4}$ s), when the role of the metal substrate as a heat sink hindering the heating of inner oxide regions becomes dominant. This leads to steep temperature gradients across the coating, which results in forsterite crystallisation and grain growth towards the surface, where thermal degradation of adsorbed HNTs particles also occurs. A good quantitative agreement between temperature distributions derived from simple thermodynamic considerations and experimentally observed coating microstructures provides an important stepping-stone on the road towards PEO process design and development of ceramic coatings with tailored properties.

- The corrosion resistance of PEO treated AM50 alloy samples increases with increased frequency of pulsed unipolar current, with little influence of the presence of HNTs. This improvement is mainly associated with the refinement of the coating morphology, providing an important pre-requisite for the achievement of yet better corrosion protection via active functionalisation of PEO coatings.

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Figure Captions

Figure 1. (a) Evolution of voltage with time for PEO treatments at different frequencies and (b) typical optical emission spectrum of plasma discharge during PEO treatment of AM50 Mg alloy with pulse frequency of 5000 Hz, with inset showing the evolution of instantaneous estimates of plasma electron temperature T_e derived from relative intensities of Mg I spectral lines at 383.8 and 518.3 nm.

Figure 2. Plan view SEM micrographs of HNT-containing PEO coatings produced at different current pulse frequencies (a) 100 Hz, (b) 500 Hz, (c) 1000 Hz and (d) 5000 Hz.

Figure 3. Cross-sectional SEM micrographs of HNT-containing PEO coatings and point EDS analysis in different coating locations produced at (a) 100 Hz, (b) 500 Hz, (c) 1000 Hz and (d) 5000 Hz.

Figure 4. (a) Pore density, (b) total porosity area fraction and (c) % of the mean average pore size of HNT-containing PEO coatings.

Figure 5. 3D Optical images of HNT-containing PEO coatings produced at different current pulse frequencies (a) 100 Hz, (b) 500 Hz, (c) 1000 Hz and (d) 5000 Hz.

Figure 6. XRD patterns of HNT-containing PEO coatings.

Figure 7. SEM micrographs of HNT-containing PEO coatings produced at (a, b) 100 Hz, (c, d) 500 Hz (e, f) 1000 Hz and (g, h) 5000 Hz frequency.

Figure 8. SEM micrographs in SE mode (a-e) of the PEO coating formed at frequency 5000 Hz showing (a) surface plane view, (b) tilted view, (c) FIB cross-section and (d-f) details of the FIB cross-section. (f) is showing region 1 in the backscattered electron mode.

Figure 9. (a) SEM micrograph (Forward Scatter Detector - FSD) of the cross-sectional TEM sample of the PEO coating formed at 100 Hz showing areas of the analysis together with band contrast and phase map resulting from TKD and elemental maps resulting from EDS analysis. (b) A detail EDS and TKD analysis together with an example of the electron backscattered patterns (EBSPs) from the region (b) and corresponding solutions using AZtec software and Mg_2SiO_4 phase.

Figure 10. (a) SEM micrograph (Forward Scatter Detector - FSD) of the cross-sectional TEM sample of the PEO coating formed at 5000 Hz showing areas of the EDS analysis, (b) and (c) show detail SEM micrograph together with elemental maps.

Figure 11. (a) Estimates of effective surface temperature T_{eff} developed during PEO treatments of AM50 Mg alloy using different durations of current pulses (b) with corresponding transient analysis showing the presence of two time constants in the heating process and (c) correlation between the distribution of forsterite grain size and T_{eff} across the coating thickness, outlining different zones of microstructural evolution in the PEO coating formed at 100 Hz.

Figure 12. Evolution of OCP values with time after immersion in aqueous 3.5 wt. % NaCl solution during (a) 2h, (b) 24h (c) 48 h and (d) 72 h and (e) surface appearance after 72h.

Figure 13. Nyquist plots of the EIS spectra of PEO coatings formed at different frequencies: (a) 100Hz, (b) 500Hz, (c) 1000Hz and (d) 5000Hz, after 2, 24, 48 and 72h of immersion in naturally aerated 3.5 wt. % NaCl solution and (e) equivalent circuit used to fit the experimental data.

Figure 14. Impedance modulus 0.1 Hz as a function of immersion time for AM50 Mg alloy samples PEO treated at different frequencies after 72 h.

Tables

Table 1. Surface EDS analysis of HNT-containing PEO coatings on AM50 Mg alloy produced at different pulse frequencies.

	Elements (at. %)							
	O	F	Na	Mg	Al	Si	K	ΔSi
100 Hz	53.2	5.0	1.3	24.0	1.5	14.9	0.2	2.9
500 Hz	56.1	5.8	1.1	23.5	1.3	12.2	0.1	0.5
1000 Hz	56.0	6.0	1.2	22.7	1.4	12.6	0.1	1.2
5000 Hz	54.8	7.9	0.8	24.3	1.3	11.0	0.1	-1.1

Table 2. Simulated parameters of EIS elements for PEO treated AM50 Mg alloy at different frequencies

Frequency (Hz)	Time (h)	$\text{CPE}_c\text{-T}$ ($\mu\text{S s}^n \text{cm}^{-2}$)	$\text{CPE}_c\text{-n}$	R_c ($\text{k}\Omega \text{cm}^2$)	L ($\text{k}\Omega \text{s cm}^{-2}$)	R_2 ($\text{k}\Omega \text{cm}^2$)
100	2	0.3	0.80	49.8	16.9	94.5
	24	4.3	0.94	8.9	12.1	25.2
	48	11.3	0.95	3.4	5.9	5.4
	72	15.0	0.93	2.8	0.8	2.8

500	2	0.3	0.75	25.7	17.0	28.6
	24	2.0	0.93	10.2	6.1	33.3
	48	14.1	0.94	1.3	1.0	1.7
	72	15.6	0.93	2.9	0.9	20.3
1000	2	1.3	0.62	56.1	8.3	72.7
	24	1.0	0.87	15.5	5.0	24.2
	48	8.6	0.93	1.7	0.6	3.6
	72	11.1	0.94	2.4	1.4	2.5
5000	2	0.2	0.81	484.3	114.6	105.3
	24	1.0	0.78	31.1	45.9	317.1
	48	4.1	0.94	4.5	3.2	1.0
	72	10.4	0.94	2.2	1.4	9.4

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Figure 10.

Figure 11.

Figure 12.

Figure 13.

Figure 14.